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The attached documents are exact copies of the European patent application conformes à la version described on the following page, as originally filed.

Les documents fixés à cette attestation sont initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Demande de brevet n° Patent application No. Patentanmeldung Nr.

99810612.4

PRIORITY DOCUMENT

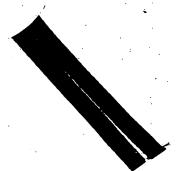
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Blatt 2 der Bescheinigung Sheet 2 of the certificate Page 2 de l'attestation

Anmeldung Nr.: Application no.: Demande n°:

99810612.4

Anmelder: Applicant(s):

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Bezeichnung der Erfindung: Title of the invention: Titre de l'invention:

Colour photographic material

Anmeldetag: Date of filing: Date de dépôt:

09/07/99

In Anspruch genommene Prioriät(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Tag: Date:

Pays:

Aktenzeichen:

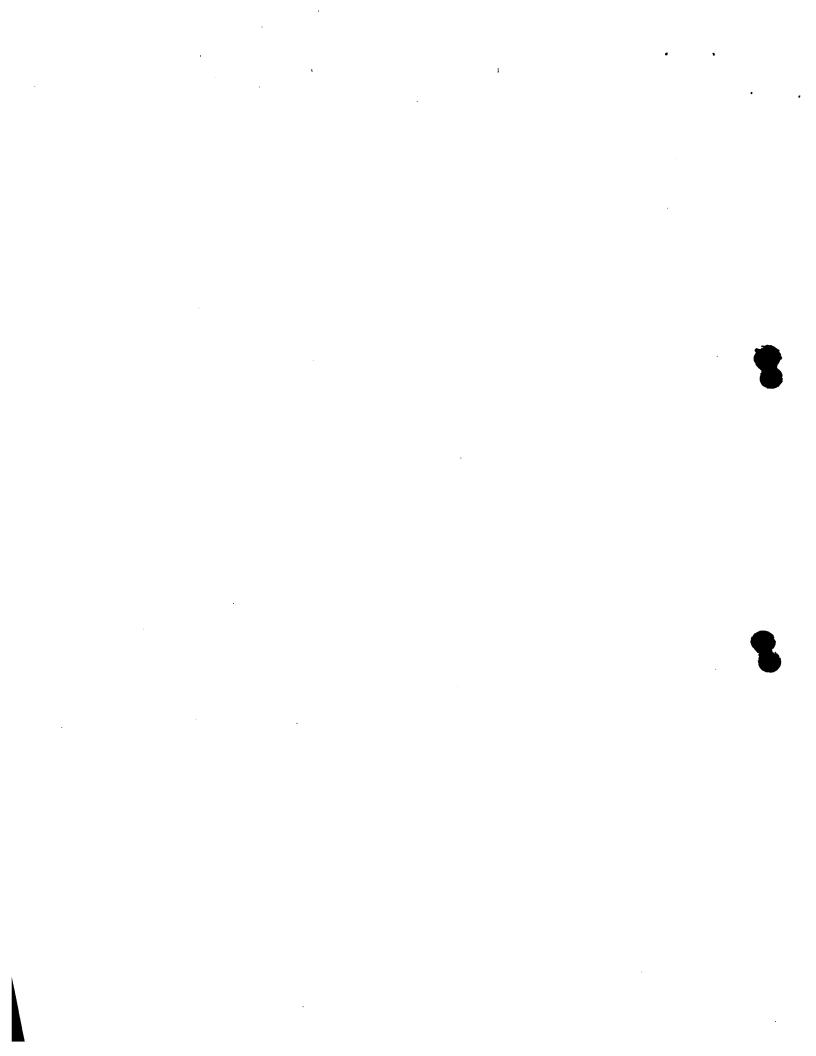
File no.

Numéro de dépôt:

Internationale Patentklassifikation: International Patent classification: Classification internationale des brevets:

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants designés lors du depôt:

Bemerkungen: Remarques:



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Colour Photographic Material

The present invention relates to colour photographic material comprising a certain lacton (benzofuran-2-one) type compound, to the use of this compound as an additive to photographic material, especially as scavenger for the oxidised form of the developer (Dox-scavenger), to some new compounds of the benzofuran-2-one class, and their use as stabilisers for organic material against oxidative, thermal and/or light-induced degradation.



It is well known that one of the problems associated with colour photography is the diffusion of the oxidised colour developer away from the light sensitive silver halide emulsion layer in which it is formed into another silver halide emulsion layer, which can result in the formation of unwanted dyes at undesired places. For instance, while being generated in the green sensitive layer and forming a magenta dye through a coupling reaction with the incorporated magenta coupler, the oxidised developer can also diffuse to the red sensitive layer thereby producing unwanted cyan dye or to the blue sensitive layer thereby producing unwanted yellow dye. This kind of colour formation in the wrong layers will damage the colour balance of the photographic image and thus result in poor colour reproduction. One way of circumventing this problem is to incorporate oxidised developer scavengers in interlayers between the light sensitive silver halide emulsion layers. These scavengers should have additional properties such as low tendency to migrate, good stability towards aerial oxidation and high solublity in photographic oils.



Several classes of compounds that are useful as scavengers for oxidised developers are known in literature, e.g. specific derivatives of hydroquinone (US-2336327, US-2732300, US-3700453, US-4345016, JP-A 83-021249, JP-A 86-083 536 and JP-A 88-046 451); hydrazines (EP-A-338 785, EP-A-679 944, US-4923 787); sulphonamidophenol (EP-A-654702, US-4447523, JP-A 85-118 835); gallic acid (US-4476219, US-4474874, JP-A 93-002 249, JP-A 86-083 536); resorcinol (US-3770431, US-3772014); catechol (US-4175969, US-4252893, EP-A-727706); aminophenol or aminonaphthol (RD 178, 94-7,1979); natural antioxidants such as vitamin E or vitamin C (US-2360290, US-2710801).

Photographic material containing a certain type of benzofuran-2-one is mentioned in US-3615521 (use as precursor of photographic developing agent) and in US-4366240 (hydroxy substituted compounds as electron donor precursors for reducible color providing

compounds). A defensive publication US 904 003 (19.11.1971) discloses some aryl-benzofuran-2-ones as competitive couplers for use in photographic developer compositions or in light sensitive silver halide emulsion layers. DE-A-197 49 083 mentions the use of a symmetrically substituted 3-(2-hydroxyphenyl)-benzofuran-2-one in the interlayer of a colour photographic material.

It has now been found that certain compounds of the 3-aryl-benzofuran-2-one class are especially useful as additives to photographic material. They are effective in a number of applications and find utility, for example, as scavengers for the oxidised developer (also termed hereafter Dox scavengers), as dye stabilisers, as antioxidants or as antifoggants. Liquid compounds of the below formula I can also be used as a photographic oil. These compounds are especially stable towards aerial oxidation, diffusion fast and also exhibit a good solubility in high boiling photographic oils. They are well suited for use in photographic elements containing pyrazolotriazole couplers as magenta dye providing compounds, since they are harmless to the light fastness of magenta images obtained from such pyrazolotriazole couplers when compared to hydroquinones.

Primary subject of the invention is a process for preventing migration of the oxidised developer in a colour photographic material from one colour sensitive layer to another by incorporating a compound of the formula I into said material

wherein, if n = 1,

R₁ is naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthala-

zinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy, halogen, amino, C_1 - C_4 alkylamino, phenylamino or di(C_1 - C_4 -alkyl)amino, or R_1 is a radical of formula II

$$\begin{array}{c}
R_{9} \\
R_{7} \\
R_{8}
\end{array}$$
(II),

and, if n = 2,

 R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxy-substituted phenylene or naphthylene; or - R_{12} -X- R_{13} - ,

 R_2 , R_3 , R_4 and R_5 are each independently of one another hydrogen, chloro, hydroxy, C_1 - C_{25} -alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 -alkyl)amino, C_1 - C_2 -alkanoyloxy, C_1 - C_2 -alkanoyloxy;

C₃-C₂₅alkanoyloxy which is interrupted by oxygen, sulfur or N-R₁₄; C₆-C₉cycloalkyl-

carbonyloxy, benzoyloxy or C_1 - C_{12} alkyl-substituted benzoyloxy; or R_2 and R_3 , or R_3 and R_4 , or R_4 and R_5 , together with the linking carbon atoms, form a benzene ring; or R_4 is $-C_mH_{2m}$ - COR_{15} or $-(CH_2)_qOH$ or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of formula III

$$R_{2}$$

$$R_{16}$$

$$C - R_{17}$$

$$(III),$$

wherein R_1 is as defined above for n = 1;

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R₆ is hydrogen or, when R₄ is hydroxy, R₆ can also be C₁-C₂₅alkyl or C₃-C₂₅alkenyl;

R₇, R₈, R₉, R₁₀ and R₁₁ are each independently of one another hydrogen, halogen, hydroxy,

C₁-C₂₅alkyl; C₂-C₂₅alkyl which is interrupted by oxygen, sulfur or N-R₁₄; C₁-C₂₅alkoxy;

C₂-C₂₅alkoxy which is interrupted by oxygen, sulfur or N-R₁₄; C₁-C₂₅alkylthio, C₃-C₂₅-

alkenyl, C_3 - C_2 salkenyloxy, C_3 - C_2 salkynyl, C_3 - C_2 salkynyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_2 salka-

noyl; C₃-C₂₅alkanoyl which is interrupted by oxygen, sulfur or N-R₁₄; C₁-C₂₅alkanoyl-

oxy; C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alka-

noylamino, C₃-C₂₅alkenoyl; C₃-C₂₅alkenoyl which is interrupted by oxygen, sulfur or

N-R₁₄; C₃-C₂₅alkenoyloxy; C₃-C₂₅alkenoyloxy which is interrupted by oxygen, sulfur or

N-R₁₄; C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-

substituted benzoyl; benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy;

R₁₁, together with the linking carbon atoms, form a benzene ring,

R₁₂ and R₁₃ are each independently of the other unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

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 R_{15} is hydroxy, $\left[-O^{-\frac{1}{r}M^{r+}}\right]$, C_1 - C_{20} alkoxy, -N R_{25} , or a group of the formula IIIa

 R_{16} and R_{17} are each independently of the other hydrogen, CF_3 , C_1 - C_{12} alkyl or phenyl, or R_{16} and R_{17} , together with the linking carbon atom, are a C_5 - C_8 cycloalkylidene ring which is unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl;

 R_{18} and R_{19} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl, R_{20} is hydrogen or C_1 - C_4 alkyl,

 R_{21} is hydrogen, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; C_1 - C_2 salkyl; C_2 - C_2 salkyl which is interrupted by oxygen, sulfur or $N-R_{14}$; C_7 - C_9 phenylalkyl which is unsubstituted or substituted at the phenyl moiety by 1 to 3 C_1 - C_4 alkyl; C_7 - C_2 sphenylalkyl which is interrupted by oxygen, sulfur or $N-R_{14}$ and which is unsubstituted or substituted at the

phenyl moiety by 1 to 3 C_1 - C_4 alkyl, or R_{20} and R_{21} , together with the linking carbon atoms, form a C_5 - C_{12} cycloalkylene ring which is unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl; R_{22} is hydrogen or C_1 - C_4 alkyl,

 R_{23} is hydrogen, C_1 - C_{25} alkanoyl, C_3 - C_{25} alkanoyl; C_3 - C_{25} alkanoyl which is interrupted by oxygen, sulfur or $N - R_{14}$; C_2 - C_{25} alkanoyl which is substituted by a di(C_1 - C_6 alkyl)phosphonate group; C_6 - C_9 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1 - C_{12} alkyl-substituted

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R₂₄ and R₂₅ are each independently of the other hydrogen or C₁-C₁₈alkyl,

R₂₆ is hydrogen or C₁-C₈alkyl,

R₂₇ is a direct bond, C₁-C₁₈alkylene; C₂-C₁₈alkylene which is interrupted by oxygen, sulfur or

N-R₁₄; C₂-C₁₈alkenylene, C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalky-

lene, C7-C8bicycloalkylene, unsubstituted or C1-C4alkyl-substituted phenylene,

$$R_{28}$$
 is hydroxy, $\left[-0^{-\frac{1}{r}M^{r+}}\right]$, C_1 - C_{18} alkoxy or $-N$
 R_{25}

R₂₉ is oxygen or -NH-,

R₃₀ is C₁-C₁₈alkyl or phenyl,

R₃₁ is hydrogen or C₁-C₁₈alkyl,

M is an r-valent metal cation,

Q is oxygen or -NH-,

X is a direct bond, oxygen, sulfur or -NR₃₁-,

Z is a linking group of valency (k+1) and is as a divalent group C_2 - C_{12} alkylene, Q-interrupted C_4 - C_{12} alkylene, phenylene or phenylene-D-phenylene with D being C_1 - C_4 alkylene, O, S, SO or SO₂;

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Z as a trivalent group is C_3 - C_{12} alkanetriyl, a trivalent residue of a hexose or a hexitol, a group $(-CH_2)_3$ C- CH_2 OH, or a group $-C_aH_{2a}$ - $N(C_bH_{2b}$ - $)-C_cH_{2c}$ -; and

Z as a tetravalent group is a tetravalent residue of a hexose or a hexitol, C₄-C₁₂alkanetetryl, a



a, b, c and k independently are 1, 2 or 3;

m is 0 or a number from the range 1-12, preferably 1-6;

n is 1 or 2:

q is 1, 2, 3, 4, 5 or 6;

r is 1, 2 or 3; and

s is 0, 1 or 2;

provided that, when R_7 is hydroxy, alkanoyloxy or alkanoyloxy interrupted by O, S or N(R_{14}) and R_9 is hydrogen, R_{10} is not identical with R_4 ; and when R_9 is hydroxy, alkanoyloxy or alkanoyloxy interrupted by O, S or N(R_{14}) and R_7 is hydrogen, R_8 is not identical with R_4 .

R₁ is preferably a radical of formula II. These preferred compounds of formula I

advantageously carry at least one hydrocarbon or substituted hydrocarbon radical R₂, R₃, R₄, R₅, R₂, R₃, R₃, R₃, R₃, R₁₀ and/or R₁₁, where the total number of carbon atoms in all radicals together is at least 3. More preferred compounds comprise one or more substituents among R₂-R₅ and R₂-R₁₁, wherein the total number of carbon atoms in all substituents together is 4-35,

especially 7-30.

Further objects of the invention are the use of a compound of the formula I in colour photographic material, especially as Dox-scavenger, and a photographic material containing a compound of the formula I, especially as herein defined below, e.g. of formula IV.

Preferred residues of the classes naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl,

cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, hydroxy, halogen, amino, C₁-C₄alkylamino, phenylamino or di(C₁-C₄alkyl)amino are, for example, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethyl-amino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-pyrrolyl, 3-pyrrolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl.

Halogen is typically chloro, bromo or iodo. Chloro is preferred.

Alkanoyl of up to 25 carbon atoms is a branched or unbranched radical, typically formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, eicosanoyl or docosanoyl. Alkanoyl of 2 to 18, in particular of 2 to 12, e.g. of 2 to 6, carbon atoms is preferred. Acetyl is particularly preferred. C₂-C₂₅Alkanoyl which is substituted by a di(C₁-C₆alkyl)phosphonate group is typically (CH₃CH₂O)₂POCH₂CO-, (CH₃O)₂POCH₂CO-, (CH₃CH₂CH₂O)₂POCH₂CO-, (CH₃CH₂O)₂POCH₂CO-, (CH₃CH₂O)₂POCH₂CO-, (CH₃CH₂O)₂POCH₂CO-, (CH₃CH₂O)₂PO(CH₂)₄CO-, (CH₃CH₂O)₂PO(CH₂)₈CO- or (CH₃CH₂O)₂PO(CH₂)₁₇CO-. C₃-C₂₅Alkanoyl which is interrupted

by oxygen, sulfur or N-R₁₄ is typically CH₃-O-CH₂CO-, CH₃-S-CH₂CO-,

CH₃-NH-CH₂CO-, CH₃-N(CH₃)-CH₂CO-, CH₃-O-CH₂CH₂-O-CH₂CO-, CH₃-(O-CH₂CH₂-)₂O-CH₂CO-, CH₃-(O-CH₂CH₂-)₃O-CH₂CO- or CH₃-(O-CH₂CH₂-)₄O-CH₂CO-.

Alkanoyloxy is oxygen-capped alkanoyl; preferences are mainly as can be derived from alkanoyl above.





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Alkenoyl of 3 to 25 carbon atoms is a branched or unbranched radical, typically propenoyl, 2-butenoyl, 3-butenoyl, isobutenoyl, n-2,4-pentadienoyl, 3-methyl-2-butenoyl, n-2-octenoyl, n-2-dodecenoyl, isododecenoyl, oleoyl, n-2-octadecenoyl or n-4-octadecenoyl. Alkenoyl of 3 to 18, preferably of 3 to 12, e.g. of 3 to 6, most preferably of 3 to 4, carbon atoms is preferred.

 C_3 - C_{25} Alkenoyl which is interrupted by oxygen, sulfur or $N-R_{14}$ is typically

CH₃OCH₂CH₂CH=CHCO- or CH₃OCH₂CH₂OCH=CHCO-.



Alkenoyloxy is oxygen-capped alkenoyl; preferences are mainly as can be derived from alkenoyl above.

C₆-C₉Cycloalkylcarbonyl is typically cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. Cyclohexylcarbonyl is preferred. C₆-C₉Cycloalkylcarbonyloxy is oxygen-capped cycloalkylcarbonoyl; preferences are analogous.

 C_1 - C_{12} Alkyl-substituted benzoyl which preferably carries 1 to 3, more preferably 1 or 2, alkyl groups is typically o-, m- or p-methylbenzoyl, 2,3-dimethylbenzoyl, 2,4-dimethylbenzoyl, 2,5-dimethylbenzoyl, 2,6-dimethylbenzoyl, 3,5-dimethylbenzoyl, 2-methyl-6-ethylbenzoyl, 4-tert-butylbenzoyl, 2-ethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,6-dimethyl-4-tert-butylbenzoyl or 3,5-di-tert-butylbenzoyl. Preferred substituents are C_1 - C_8 alkyl, in particular C_1 - C_4 alkyl.



 C_1 - C_{12} Alkyl-substituted benzoyloxy which preferably carries 1 to 3, more preferably 1 or 2, alkyl groups is typically o-, m- or p-methylbenzoyloxy, 2,3-dimethylbenzoyloxy, 2,4-dimethylbenzoyloxy, 3,4-dimethylbenzoyloxy, 3,5-dimethylbenzoyloxy, 2-methyl-6-ethylbenzoyloxy, 4-tert-butylbenzoyloxy, 2-ethylbenzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-di-tert-butylbenzoyloxy. Preferred substituents are C_1 - C_8 alkyl, in particular C_1 - C_4 alkyl.

Alkyl of up to 25 carbon atoms is a branched or unbranched radical, such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylh xyl, tridecyl, tetrad cyl, p ntadecyl, hexadecyl, h ptad cyl, octad cyl, eicosyl or do-

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cosyl. One of the preferred meanings of R_2 and R_4 is, for example, C_1 - C_{18} alkyl. A particularly preferred meaning of R_4 is C_1 - C_4 alkyl. One of R_2 and R_4 is preferably a branched radical; especially preferred are both R_2 and R_4 branched radicals.

Alkenyl of 3 to 25 carbon atoms is a branched or unbranched radical, such as propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, isododecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Alkenyl of 3 to 18, preferably of 3 to 12, e.g. of 3 to 6, in particular of 3 to 4, carbon atoms is preferred.

Alkenyloxy is oxygen capped alkenyl; preferences are analogous.

Alkynyl of 3 to 25 carbon atoms is a branched or unbranched radical, such as propynyl (—CH₂-C=CH), 2-butynyl, 3-butynyl, n-2-octynyl, or n-2-dodecynyl. Alkynyl of 3 to 18, preferably of 3 to 12, e.g. of 3 to 6, in particular of 3 to 4 carbon atoms is preferred. Preferences for alkynyloxy (oxygen capped alkynyl) are analogous.

C₂-C₂₅Alkyl which is interrupted by oxygen, sulfur or N-R₁₄ is typically

 C_7 - C_9 Phenylalkyl is typically benzyl, α -methylbenzyl, α , α -dimethylbenzyl or 2-phenylethyl. Benzyl and α , α -dimethylbenzyl are preferred.

 C_7 - C_9 Phenylalkyl which is unsubstituted or substituted at the phenyl moiety by 1 to 3 C_1 - C_4 -alkyl is typically benzyl, α -methylbenzyl, α , α -dimethylbenzyl, 2-phenylethyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2,6-dimethylbenzyl or 4-tert-butylbenzyl. Benzyl is preferred.

C₇-C₂₅Phenylalkyl which is interrupted by oxygen, sulfur or N-R₁₄ and which is unsub-

stituted or substituted at the phenyl moiety by 1 to 3 C₁-C₄alkyl is a branched or unbranched radical, such as phenoxymethyl, 2-methylphenoxymethyl, 3-methyl-phenoxymethyl, 4-me-

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thylphenoxymethyl, 2,4-dimethylphenoxymethyl, 2,3-dimethylphenoxymethyl, phenylthiomethyl, N-methyl-N-phenyl-methyl, N-ethyl-N-phenylmethyl, 4-tert-butylphenoxymethyl, 4-tert-butylphenoxymethyl, 2,4-di-tert-butylphenoxymethyl, 2,4-di-tert-butylphenoxymethyl, benzyloxymethyl, benzyloxymethyl, N-benzyl-N-ethylmethyl or N-benzyl-N-isopropylmethyl.

 C_7 - C_9 Phenylalkoxy is typically benzyloxy, α -methylbenzyloxy, α , α -dimethylbenzyloxy or 2-phenylethoxy. Benzyloxy is preferred.



C₁-C₄Alkyl-substituted phenyl which preferably contains 1 to 3, in particular 1 or 2, alkyl groups is typically o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methylphenyl, phenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

C₁-C₄Alkyl-substituted phenoxy which preferably contains 1 to 3, in particular 1 or 2, alkyl groups is typically o-, m- or p-methylphenoxy, 2,3-dimethylphenoxy, 2,4-dimethylphenoxy, 2,5-dimethylphenoxy, 2,6-dimethylphenoxy, 3,4-dimethylphenoxy, 3,5-dimethylphenoxy, 2-methyl-6-ethylphenoxy, 4-tert-butylphenoxy, 2-ethylphenoxy or 2,6-diethylphenoxy.



Unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl is, for example, cyclopentyl, methyl-cyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethyl-cyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. Cyclohexyl and tert-butylcyclohexyl are preferred.

Unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy is, for example, cyclopentoxy, methylcyclopentoxy, dimethylcyclopentoxy, methylcyclohexoxy, dimethylcyclohexoxy, dimethylcyclohexoxy, tert-butylcyclohexoxy, cycloheptoxy or cyclooctoxy. Cyclohexoxy and tert-butylcyclohexoxy are preferred.

Alkoxy of up to 25 carbon atoms is a branched or unbranched radical, such as methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Alkoxy of 1 to 12, in particular of 1 to 8, e.g. of 1 to 6, carbon atoms is preferred.



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 C_2 - C_{25} Alkoxy which is interrupted by oxygen, sulfur or $N-R_{14}$ is typically

 $CH_{3}-O-CH_{2}CH_{2}O-,\ CH_{3}-S-CH_{2}CH_{2}O-,\ CH_{3}-NH-CH_{2}CH_{2}O-,\ CH_{3}-N(CH_{3})-CH_{2}CH_{2}O-,\ CH_{3}-O-CH_{2}CH_{2}-O-CH_{2}CH_{2}O-,\ CH_{3}-(O-CH_{2}CH_{2}-)_{2}O-CH_{2}CH_{2}O-,\ CH_{3}-(O-CH_{2}CH_{2}-)_{3}O-CH_{2}CH_{2}O-\ or\ CH_{3}-(O-CH_{2}CH_{2}-)_{4}O-CH_{2}CH_{2}O-.$

Alkylthio of up to 25 carbon atoms is a branched or unbranched radical, such as methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio, heptylthio, octylthio, decylthio, tetradecylthio, hexadecylthio or octadecylthio. Alkylthio of 1 to 12, in particular of 1 to 8, e.g. of 1 to 6 carbon atoms is preferred.

Alkylamino of up to 4 carbon atoms is a branched or unbranched radical, such as methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutylamino or tert-butylamino.

Di(C₁-C₄alkyl)amino also means that the two radicals are independently of the other branched or unbranched, such as dimethylamino, methylethylamino, diethylamino, methyl-n-propylamino, methylisopropylamino, methyl-n-butylamino, methylisobutylamino, ethylisopropylamino, ethyl-n-butylamino, ethylisobutylamino, diethylamino, diethylamino, diisopropylamino, isopropyl-n-butylamino, isopropylisobutylamino, di-n-butylamino or di-isobutylamino.

Alkanoylamino of up to 25 carbon atoms is a branched or unbranched radical, such as formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, hexanoylamino, hexanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino, hexadecanoylamino, heptadecanoylamino, octadecanoyamino, eicosanoylamino or docsanoylamino. Alkanoylamino of 2 to 18, in particular of 2 to 12, e.g. of 2 to 6, carbon atoms is preferred.

 C_1 - C_{18} Alkylene is a branched or unbranched radical, such as methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene. C_1 - C_{12} Alkylene and, in particular, C_1 - C_8 alkylene are preferred.





A C₁-C₄Alkyl-substituted C₅-C₁₂cycloalkylene ring which preferably contains 1 to 3, in particular 1 or 2, branched or unbranched alkyl groups is typically cyclopentylene, methylcyclopentylene, dimethylcyclopentylene, cyclohexylene, methylcyclohexylene, dimethylcyclohexylene, trimethylcyclohexylene, tert-butylcyclohexylene, cycloheptylene, cyclooctylene or cyclodecylene. Cyclohexylene and tert-butylcyclohexylene are preferred.

C₂-C₁₈Alkylene which is interrupted by oxygen, sulfur or N-R₁₄ is, for example,



 $-CH_2-O-CH_2-, -CH_2-S-CH_2-, -CH_2-NH-CH_2-, -CH_2-N(CH_3)-CH_2-, -CH_2-O-CH_2CH_2-O-CH_2-, -CH_2-(O-CH_2CH_2-)_2O-CH_2-, -CH_2-(O-CH_2CH_2-)_3O-CH_2-, -CH_2-(O-CH_2CH_2-)_4O-CH_2- or$

-CH₂-(O-CH₂CH₂-)₂O-CH₂-, -CH₂-(O-CH₂CH₂-)₃O-CH₂-, -CH₂-(O-CH₂CH₂-)₄O-CH₂- or -CH₂CH₂-S-CH₂CH₂-.

 C_2 - C_{18} Alkenylene is typically vinylene, methylvinylene, octenylethylene or dodecenylethylene. C_2 - C_8 Alkenylene is preferred.

Alkylidene of 2 to 20 carbon atoms is, for example, ethylidene, propylidene, butylidene, pentylidene, 4-methylpentylidene, heptylidene, nonylidene, tridecylidene, nonadecylidene, 1-methylethylidene, 1-ethylpropylidene or 1-ethylpentylidene. C₂-C₈Alkylidene is preferred.



Phenylalkylidene of 7 to 20 carbon atoms is typically benzylidene, 2-phenylethylidene or 1-phenyl-2-hexylidene. C₇-C₉Phenylalkylidene is preferred.

 C_5 - C_8 Cycloalkylene is a saturated hydrocarbon group having two free valencies and at least one ring unit and is typically cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene. Cyclohexylene is preferred.

 $C_7\text{-}C_8$ Bicycloalkylene is typically bicycloheptylene or bicyclooctylene.

Unsubstituted or C_1 - C_4 alkyl-substituted phenylene or naphthylene is typically 1,2-, 1,3-, 1,4-phenylene, 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, 2,6- or 2,7-naphthylene. 1,4-Phenylene is preferred.

A C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyliden ring which preferably contains 1 to 3, in particular 1 or 2, branched or unbranched alkyl groups is typically cyclopentylidene, methylcyclopentylidene, cyclohexylidene, methylcyclohexylidene, dimethylcyclopentylidene, dimethylcyclohexylidene, dimethylcyclopentylidene, dimethylcyclohexylidene, dimethylcyclopentylidene, dime

lohexylidene, trimethylcyclohexylidene, tert-butylcyclohexylidene, cycloheptylidene or cyclooctylidene. Cyclohexylidene and tert-butylcyclohexylidene are preferred.

A mono-, di- or tri-valent metal cation is preferably an alkali metal cation, alkaline earth metal cation or aluminium cation, typically Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺ or Al⁺⁺⁺.

Preferred are compositions containing a compound of formula I, wherein R_2 , R_3 and R_5 , independently, are H, CI, hydroxy, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; C_1 - C_{18} alkoxy, C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkenoyloxy; and where

 R_4 is CI, hydroxy, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; C_1 - C_{18} alkoxy, C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkenoyloxy or is a group - C_mH_{2m} - COR_{15} , or where R_3 , R_5 and R_6 are H, R_4 may be a residue of formula III, or where R_8 or R_{10} are other than H, R_4 may also be hydrogen;

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently are H, halogen, hydroxy, C_1 - C_{25} alkyl, O interrupted C_2 - C_{25} alkyl; C_1 - C_{25} alkoxy, O interrupted C_2 - C_{25} alkoxy, C_3 - C_{25} alkenyl, C_3 - C_{25} alkenyloxy, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl substituted phenoxy; unsubstituted or C_1 - C_4 alkyl substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl substituted C_5 - C_8 cycloalkyl)amino, C_1 - C_{25} alkanoyl; C_1 - C_{25} alkanoyloxy; C_6 - C_9 cycloalkylcarbonyl, C_8 - C_9 cycloalkylcarbonyloxy, benzoyl or C_1 - C_{12} alkyl-substituted benzoyl; benzoyloxy or C_1 -

C₁₂alkyl substituted benzoyloxy;
$$-O - \overset{R_{18}}{\overset{1}{\text{C}}} \overset{O}{\overset{1}{\text{C}}} - R_{15} \quad \text{or} \quad -O - \overset{R_{20}}{\overset{1}{\text{C}}} - \overset{R_{21}}{\overset{1}{\text{C}}} - O - R_{23} \quad \text{, or}$$

where in formula II R_7 and R_8 or R_8 and R_{11} together with the carbon atoms, they are bonded to, form a phenyl ring;

$$R_{15}$$
 is C_1 - C_{18} alkoxy or N
 R_{25}
or a group of formula IIIa;



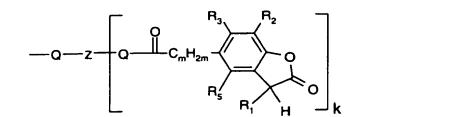


R₆ is H.

(IIIa);



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 R_{16} and R_{17} independently are H, CF_3 , C_1 - C_{12} alkyl or phenyl; or R_{16} and R_{17} together with the bonding carbon atom form an unsubstituted or 1-3 C_1 - C_4 alkyl-substituted C_5 -

Cacycloalkylidene ring;

R₁₈ and R₁₉ independently are H, C₁-C₄ alkyl or phenyl;

R₂₀ is H or C₁-C₄alkyl;

 R_{21} is H, unsubstituted or C_1 - C_4 alkyl substituted phenyl; C_1 - C_{25} alkyl, unsubstituted or on the phenyl ring 1-3 C_1 - C_4 alkyl-substituted C_7 - C_9 phenylalkyl;

R₂₂ is H or C₁-C₄alkyl;

 R_{23} is H, C_1 - C_{25} alkanoyl, C_3 - C_{25} alkenoyl; di(C_1 - C_6 alkyl)phosphonate-substituted C_2 - C_{25} alkanoyl; C_6 - C_9 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1 - C_{12} alkyl-substituted

benzoyl;
$$\bigcap_{C \to C_8 H_{28}} \bigoplus_{C \to C_8 H_{28}} \bigoplus_$$

 R_{24} and R_{25} independently are H or C_1 - C_{18} alkyl;

R₂₆ is H or C₁-C₈alkyl;

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R₂₇ is a direct bond, C₁-C₁₈alkylen, C₂-C₁₈alkenylen, C₇-C₂₀phenylalkyliden, C₅-

 $C_{\theta} cycloal kylen, \ unsubstituted \ or \ C_{1}\text{-}C_{4} alkyl\text{-}substituted \ phenylene,}$

$$\sqrt{s}$$
:

R₂₉ is O or -NH-;

R₃₀ C₁-C₁₈alkyl or phenyl:

M a metal cation of the valency r;

X a direct bond, O, S or -NR₃₁-;

n 1 or 2;

m is a number from the range 1-8;

q 1, 2, 3, 4, 5 or 6;

r 1, 2 or 3; and

s is 0, 1 or 2.

More preferred for use according to present invention is a compound of the formula IV

wherein

R₂ is H or C₁-C₂₀alkyl;

R₃ is H or C₁-C₁₈alkyl;

R4 is C1-C8alkyl, H, C1-C6alkoxy or a group -CmH2m-COR15 or a group of the formula III

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$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ R_{\overline{16}} & C - R_{17} & \end{array}$$
 (III);

R₅ is H or C₁-C₁₈alkyl;

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently are H, OH, chloro, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, di(C_1 - C_4 alkyl)amino, phenyl, C_2 - C_{18} alkanoyloxy, C_3 - C_{18} -alkoxycarbonylalkoxy or

especially wherein at least 2 of the residues R7, R8, R9, R10, R11 are H;

R₁₅ is C₁-C₁₈alkoxy or a group of the formula IIIa

$$-Q-z = \begin{bmatrix} O & R_3 & R_2 \\ O & C_m H_{2m} & O \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

 R_{16} and R_{17} independently are H, C_1 - C_{12} alkyl or phenyl; or R_{16} and R_{17} together with the bonding carbon atom form a C_5 - C_8 cycloalkylidene ring;

R₂₀, R₂₁ and R₂₂ independently are H or C₁-C₄alkyl;

$$H_3C$$
 CH_3
 CH_3

R₂₆ is C₁-C₄alkyl;

Q is oxygen;

Z is C₂-C₁₂alkylene;

k is 1;

m is 1, 2, 3, 4, 5 or 6 and

s is 0, 1 or 2.

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 R_4 is preferably not H, most preferably not H and not OH. Especially preferred is a compound wherein R_4 is C_1 - C_6 alkyl, especially tertiary C_4 - C_6 alkyl, or a group - C_mH_{2m} - COR_{15} or a group of the formula III.

Most preferred for use according to present invention is a compound of the formula IV wherein

R2 is C1-C20alkyl;

R₃ is H or C₁-C₁₈alkyl;

 R_4 is C_1 - C_6 alkyl, C_1 - C_6 alkoxy or a group - C_mH_{2m} - COR_{15} or a group of the formula III

$$R_{2}$$

$$R_{16}$$

$$R_{16}$$

$$R_{17}$$

$$R_{17}$$

$$R_{18}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

R₅ is H or C₁-C₁₈alkyl;

R₇ and R₉ independently are H, chloro, C₁-C₁₈alkyl;

R₈, R₁₀ and R₁₁ independently are H, OH, chloro, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, di(C₁-

$$R_{20}$$
 R_{21} R_{20} R_{21} R_{20} R_{21} R_{20} R_{21} R_{22} R_{22}

R₁₅ is C₁-C₁₈alkoxy or a group of the formula IIIa

$$-Q-z = \begin{bmatrix} Q & R_3 & R_2 \\ Q & C_m H_{2m} & Q \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

R₂₀, R₂₁ and R₂₂ are H;

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$$H_3C$$
 CH_3
 CH_3
 CH_3
 CH_2
 CH_3
 CH_3

R₂₆ is C₁-C₄alkyl;

Q is oxygen;

Z is C2-C12alkylene;

k is 1;

m is 1, 2, 3, 4, 5 or 6 and

s is 0, 1 or 2.

Of special interest are those compounds of formula IV wherein R₇ is H and R₉ is H or methyl.

More interesting is a process where in the compound of formula I, if n = 1, R_1 is phenyl which is unsubstituted or substituted in para-position by C_1 - C_{18} alkylthio or di(C_1 - C_4 -alkyl)amino; monoto penta-substituted alkylphenyl containing together a total of at most 18 carbon atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothiazinyl or 5,6,7,8-tetrahydronaphthyl which are unsubstituted or substituted by C_1 - C_4 -alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy or amino.



Also preferred compositions contain compounds of the formula I wherein the bonding atom in R_2 is a secondary or tertiary carbon atom, especially wherein R_2 is secondary C_6 - C_{22} alkyl or tertiary C_4 - C_{22} alkyl or phenyl or substituted phenyl or alkyl or alkoxy interrupted by COO; R_4 is secondary C_6 - C_{22} alkyl or tertiary C_4 - C_{22} alkyl or a group of formula III or alkyl or alkoxy interrupted by COO; and R_{11} is H or methyl or phenyl or alkyl or alkoxy interrupted by COO. Of special interest are compounds whose residues R_2 , R_4 or R_{11} contain an ester group.

Especially preferred are compounds of the formula IV wherein

R2 is H or C1-C20alkyl;

R₃ is H or C₁-C₁₈alkyl;

 R_4 is C_1 - C_6 alkyl, -(CH₂)₀-COR₁₅ or -C(CH₃)₂-(CH₂)₀-COR₁₅;

R₅ is H or C₁-C₁₈alkyl;

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 R_7 , R_8 , R_9 , R_{10} and R_{11} independently are H, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy or

especially wherein at least 2 of the residues R7, R8, R9, R10, R11 are H;

R₁₅ is C₁-C₁₈alkoxy;

R₂₀, R₂₁ and R₂₂ are H; and

p is 2 or 3.

Compounds of the formula I or IV can be obtained according to methods known in the art, e.g. as described in GB-A-2281910 or publications cited therein, or, like compounds of formula V, in analogy to those methods. Some compounds of the formula I are commercially available.

This class of lactones are preferably used to trap the oxidised form of a developer having the following general structure:

where

 $A = C_1 - C_6 - Alkyl;$

n = 1 - 6:

 $X = Hydrogen, Hydroxy, C_1-C_8-Alkoxy, COR_{15}, NHSO_2R_{30};$

 $Y = C_1 - C_8$ alkyl, $C_1 - C_8$ alkoxy, halogen; m = 0 - 4.

In the above structure the preferred substituents are $A = -CH_2CH_3$ and n=2, $X = hydrogen or -NHSO_2CH_3 or -OH or -OCH_3, <math>Y = hydrogen or -CH_3$ and m = 1.

The photographic materials according to this invention comprise a support bearing at least one layer of a light-sensitive silver halide emulsion.

Examples of colour photographic materials according to this invention are colour negative films, colour reversal films, colour photographic paper, colour reversal

photographic paper, colour-sensitive materials for the dye diffusion transfer process or the silver dye bleach process.

Of especial interest is a colour photographic recording material comprising, on a base, at least one blue-sensitive silver halide emulsion layer containing at least one yellow dye providing compound, at least one green-sensitive silver halide emulsion layer containing at least one magenta dye providing compound, at least one red-sensitive silver halide emulsion layer containing at least one cyan dye providing compound, and customary (non light sensitive) top layer(s) and interlayers separating the light-sensitive layers.

The layers of the colour photographic material can be arranged in various orders as is well

The compound of the formula I or IV can be contained in any of the layers of the photographic material, i.e. in any of the light sensitive silver halide emulsion layers or in a non light sensitive layer. For use as a Dox scavenger, the compound of the formula I is preferably contained in one or more non light sensitive layers. In this case, the light sensitive layers may contain a lower concentration of the compound of the formula I or none.

In general, the compounds of the formula I or IV are contained in the photographic material in an amount from 10 to 1000 mg/m², especially from 30 to 500 mg/m².

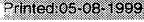
The lactones of formula I or IV can be milled with polymers (e.g. PVS, polyester, polyvinyl alcohol etc.) and placed in a layer thus preventing its migration to adjacent layers. Also, the benzofuranones containing a suitable functional group (e.g. ester, hydroxy) can be reacted with a polymer, e.g. a polyvinyl alcohol or polyester, in order to attach them chemically. This form will reduce their migrating tendency.

Typical bases for the photographic material include polymeric films and paper (including polymer-coated paper). Details regarding supports and other layers of colour photographic recording materials can be found in <u>Research Disclosure</u>, Item 36544, September 1994.

Essential constituents of the photographic emulsion layers are binders, silver halide particles and colour couplers. Details regarding the constituents of the light sensitive layers and other (non light sensitive) lay rs such as top layers and interlayers separating the silver halide emulsion layers can be found in <u>Research Disclosure</u>, Item 38957, September 1996.



known in the art.



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The invention therefore also pertains to a colour photographic material comprising a compound of the formula I or IV, and to the use of a compound of the formula I or IV as an additive in a colour photographic material.

Preferred compounds of the formula I or IV in the colour photographic material of the invention or the corresponding use are as described for the process of the invention.

Compounds of present invention are with special advantage when incorporated into photographic materials containing magenta couplers of the pyrazolotriazole class.

Examples for especially suitable yellow, magenta and cyan couplers to be used in combination with compounds of the present invention are given below:

Yellow couplers which can be used in the novel material are preferably compounds of the formula A

in which R_1 is alkyl or aryl, R_2 is aryl and Q is hydrogen or a group which can be eliminated by reaction with the oxidized developer.

One group of yellow couplers comprises those compounds of the formula A in which R_1 is t-butyl and R_2 is a group of the formula

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in which R₃ is hydrogen, halogen, alkyl or alkoxy and R₄, R₅ and R₆ are hydrogen, halogen, alkyl, alkenyl, alkoxy, aryl, carboxyl, alkoxycarbonyl, a carbamoyl group, a sulfonyl or sulfamoyl group, an alkylsulfonamino group, acylamino group, ureido group or amino group.

Preferably, R_3 is chlorine, R_4 and R_5 are hydrogen and R_6 is an acylamino group. This also includes the compounds of the formula

$$(CH_3)_3C-CO-CH-CO-NH- R_5$$
 R_8
 R_8

in which x is 0-4, R₇ is hydrogen or alkyl and R₈ and R₉ are alkyl.

Another group of yellow couplers conforms to the formula B

$$R_1COCH(Q)CONH$$
 R_{11}
 R_{12}
 R_{13}
 R_{13}
 R_{12}
 R_{13}

in which R₁₀ is hydrogen, halogen or alkoxy,

 R_{11} , R_{12} and R_{13} are hydrogen, halogen, alkyl, alkenyl, alkoxy, aryl, carboxyl, alkoxycarbonyl, a carbamoyl group, a sulfonyl group, a sulfamoyl group, sulfonamido group, acylamino group, ureido group or amino group and R_1 and Q are as defined above.

This group includes compounds of the formula B in which R_1 is t-butyl, R_{10} is chlorine, R_{11} and R_{13} are hydrogen and R_{12} is alkoxycarbonyl.

In the compounds of the formulae A and B the leaving group Q can be hydrogen or is a heterocyclic group

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in which R_{14} is a divalent organic group which supplements the ring to make up a 4-7-membered ring, or Q is a group -OR₁₅ in which R_{15} is alkyl, aryl, acyl or a heterocyclic radical.

Typical examples of customary yellow couplers are the compounds of the following formulae:

$$(CH_3)_3C-CO-CH-CONH \longrightarrow \\ NHCO(CH_2)_3O \longrightarrow \\ t-C_5H_{11} \longrightarrow \\ t-C_5H_{12} \longrightarrow \\ t-C_5H_{13} \longrightarrow \\ t-C_5H_{14} \longrightarrow \\ t$$

a)
$$Q = -O - OCH_2C_6H_5$$

b)
$$Q = -N$$

$$O = -N - CH_2C_6H_5$$

c)
$$Q = {}^{N} = \langle CH(CH_3)_2 \rangle$$

$$S = {}^{N} = \langle S \rangle$$

$$N-SO_2 - CH_3$$

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$$P \quad e) \quad Q = -N \qquad N$$

$$(CH_3)_3C - CO - CH - CONH - C_2H_5 t - C_5H_{11}$$

$$NHCO - CH - O - C_5H_{11}$$

f)
$$Q = -N$$
O
 CH_3
 CH_3

g)
$$Q = -N$$
 N -Benzyl

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h)
$$Q = -N$$

$$| S - CH(CH_3)_2$$

$$| S - CH_3$$

$$| CH_3 - CH_3$$

Further examples of yellow couplers are given in US-A 2,407,210, 2,778,658, 2,875,057, 2,908,513, 2,908,573, 3,227,155, 3,227,550, 3,253,924, 3,265,506, 3,277,155, 3,408,194, 3,341,331, 3,369,895, 3,384,657, 3,415,652, 3,447,928, 3,551,155, 3,582,322, 3,725,072, 3,891,445, 3,933,501, 4,115,121, 4,401,752 and 4,022,620, in DE-A 1,547,868, 2,057,941, 2,162,899, 2,163,813, 2,213,461, 2,219,917, 2,261,361, 2,261,362, 2,263,875, 2,329,587, 2,414,006 and 2,422,812, in GB-A 1,425,020 and 1,077,874 and in JP-A-88/123,047 and in EP-A-447,969.

The yellow couplers are customarily used in an amount of 0.05-2 mol and preferably 0.1-1 mol per mole of silver halide.

Typical and preferred yellow couplers conform to the formulae:

$$\begin{array}{c} CH_3 \\ CH_3 \\ CCH_3 \\ CH_{3} \\ CCH_{3} \\ CCH_{2} \\ CCH_{2}$$

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$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{O} \\ \text{NH-CO-(CH}_2)_3 \\ \text{O} \\ \text{SO}_2 \\ \text{OCH}_2 \\ \text{O} \\ \text{O} \\ \text{CH}_3 \\ \text{O} \\$$

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$$(Y-5) \begin{array}{c} CH_3 \\ CH_4 \\ CH_3 \\ CH_4 \\ CH_5 \\ CH_$$

$$\begin{array}{c} \text{CH}_{3} & \text{OC}_{16}\text{H}_{37} \\ \text{CH}_{3} - \text{C-CO-CHCONH} \\ \text{CH}_{3} & \text{N} \\ \text{SO}_{2}\text{NHCOC}_{2}\text{H}_{5} \end{array}$$

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Magenta couplers may, for example, be simple 1-aryl-5-pyrazolones or may be pyrazole derivatives which are fused with 5-membered heterocyclic rings, examples being imidazo-pyrazoles, pyrazolopyrazoles, pyrazolotriazoles or pyrazolotetrazoles.

One group of magenta couplers comprises 5-pyrazolones of the formula C

as are described in British Patent 2,003,473. In this formula, R₁₆ is hydrogen, alkyl, aryl,



alkenyl or a heterocyclic group, R_{17} is hydrogen, alkyl, aryl, a heterocyclic group, an ester group, alkoxy group, alkylthio group, carboxyl group, arylamino group, acylamino group, (thio)urea group, (thio)carbamoyl group, guanidino group or sulfonamido group.

$$R_{17}$$
 is preferably a group R_{18} R_{19}

in which R_{18} is imino, acylamino or ureido, R_{19} is hydrogen, halogen, alkyl or alkoxy, R_{20} is hydrogen, alkyl, acylamino, carbamoyl, sulfamoyl, sulfonamido, alkoxycarbonyl, acyloxy or a urethane group.

If Q' is hydrogen, then the magenta coupler is tetraequivalent in relation to the silver halide.

Typical examples of this type of magenta coupler are compounds of the formula

in which R_{20} is as defined above and Q', as described above, is a leaving group. These compounds are preferably present in the material of this novel process.

Further examples of such tetraequivalent magenta couplers are given in US-A 2,983,608, 3,061,432, 3,062,653, 3,127,269, 3,152,896, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,684,514, 3,834,908, 3,888,680, 3,891,445, 3,907,571, 3,928,044, 3,930,861, 3,930,866 and 3,933,500 and in JP-A-89/309,058.

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If Q' in formula C is not hydrogen but a group which is eliminated in reaction with the oxidized developer, then the magenta coupler is diequivalent. In this case Q may for example be halogen or a group which is attached via O, S or N to the pyrazole ring. Diequivalent couplers of this kind give rise to a higher colour density and are more reactive with respect to the oxidized developer than are the corresponding tetraequivalent magenta couplers.

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Examples of diequivalent magenta couplers are described in US-A 3,006,579, 3,419,391, 3,311,476, 3,432,521, 3,214,437, 4,032,346, 3,701,783, 4,351,897, 3,227,554, in EP-A-133,503, DE-A-2,944,601, JP-A-78/34044, 74/53435, 74/53436, 75/53372 and 75/122935.

Typical and preferred magenta couplers conform to the formulae



$$(M-4) \qquad \begin{matrix} C(CH_3)_2 \\ C(CH_3)_3 \end{matrix} \qquad \begin{matrix} CI \\ NH-CO-(CH_2)_{12}CH_3 \end{matrix}$$

It is possible for 2 pyrazolone rings to be linked via a divalent Q', giving so-called biscouplers. These are described, for example, in US-A-2,632,702, US-A-2,618,864, GB-A-968,461, GB-A-786,859, JP-A-76/37646, 59/4086, 69/16110, 69/26589, 74/37854 and 74/29638. Y is preferably an O-alkoxyarylthio group.

As mentioned above, the magenta couplers used can also be pyrazoles fused with 5-membered heterocycles, and are then known as pyrazoloazoles. Their advantages over simple pyrazoles are that they possess colours of greater formalin resistance and have purer absorption spectra.

Magenta couplers of the pyrazoloazole type which are likewise preferred may be represented by the formula

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in which R₁ is hydrogen or a substituent, Z represents the non-metallic atoms necessary to complete a 5-membered ring containing 2 or 3 nitrogen atoms, which ring may be substituted, and Q is hydrogen or a leaving group.

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Of these compounds, preference is given to magenta couplers of the formulae



R₁₁, R₁₂ and R₁₃ independently of one another are, for example, hydrogen, halogen, a group of the formula -CR₃ in which the radicals R, independently of one another, are hydrogen or alkyl, or aryl, heterocyclyl, cyano, hydroxyl, nitro, carboxyl, amino, alkoxy, aryloxy, acylamino, alkylamino, anilino, ureido, sulfamoylamino, alkylthio, arylthio, alkoxycarbonylamino, sulfonamido, carbamoyl, sulfamoyl, sulfonyl, alkoxycarbonyl, heterocyclyloxy, azo, acyloxy, carbamoyloxy, silyloxy, aryloxycarbonylamino, imido, heterocyclic ring-thio, sulfinyl, phosphonyl, aryloxycarbonyl, acyl or azolyl, and preferably hydrogen; halogen (e.g. chlorine, bromine), a group of the formula -CR₃ in which the radicals R independently of one another are hydrogen or alkyl, or aralkyl, alkenyl, alkynyl, cycloalkyl or cycloalkenyl, and particularly preferably methyl, ethyl, propyl, isopropyl, t-butyl, tridecyl, 2-methanesulfonylethyl, 3-(3-pentadecylphenoxy)propyl,

3-(4-(2-(4-(4-hydroxyphenylsulfonyl)phenoxy)dodecaneamido)phenyl)propyl, 2-ethoxytridecyl, trifluoromethyl, cyclopentyl, 3-(2,4-di-t-amylphenoxy)propyl); aryl (e.g. phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl, 4-tetradecanamidophenyl); heterocyclyl (e.g. 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl); cyano; hydroxyl, nitro; carboxyl; amino;

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alkoxy (e.g. methoxy, ethoxy, 2-methoxyethoxy; 2-dodecylethoxy, 2-methanesulfonylethoxy); aryloxy (e.g. phenoxy, 2-methylphenoxy, 4-t-butylphenoxy, 3-nitrophenoxy, 3-t-butyloxycarbamoylphenoxy, 3-methoxycarbamoyl); acylamino (e.g. acetamido, benzamido, tetradecaneamido, 2-(2,4-di-t-amylphenoxy)butaneamido, 4-(3-t-butyl-4-hydroxyphenoxy)butaneamido, 2-(4-(4-hydroxyphenylsulfonyl)phenoxy)decaneamido); methylbutylamino); anilino (e.g. phenylamino, 2-chloroanilino, 2-chloro-5-tetradecaneaminoanilino, 2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino, 2-chloro-5-(alpha-(3-t-butyl-4-hydroxyphenoxy)dodecaneamidoanilino); ureido (e.g. phenylureido, methylureido, N,N-dibutylureido); sulfamoylamino (e.g. N,N-dipropylsulfamoylamino, N-methyl-N-decylsulfamoylamino); alkylthio (e.g. methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, 3-(4-t-butylphenoxy)propylthio); arylthio (e.g. phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, 4-tetradecaneamidophenylthio); alkoxycarbonylamino (e.g. methoxycarbonylamino, tetradecyloxycarbonylamino); sulfonamido (e.g. methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido, 2-methyloxy-5-t-butylbenzenesulfonamido); carbamoyl (e.g. N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, N-(3-(2,4-di-tamylphenoxy)propyl)carbamoyl); sulfamoyl (e.g. N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-2(-dodecyloxyethyl)sulfamoyl, N-ethyl-N-dodecylsulfamoyl, N,N-diethylsulfamoyl); sulfonyl (.g. methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl); alkoxycarbonyl (e.g. methoxycarbonyl, butoxycarbonyl, dodecyloxycarbonyl, octadecyloxycarbonyl); heterocyclic ring-oxy (e.g. 1-phenyltetrazole-5-oxy, 2-tetrahydropyranyloxy); azo (e.g. phenylazo, 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-hydroxy-4-propanoylphenylazo); acyloxy (e.g. acetoxy); carbamoyloxy (e.g. N-methylcarbamoyloxy, N-phenylcarbamoyloxy); silyloxy (e.g. trimethylsilyloxy, dibutylmethylsilyloxy); aryloxycarbonylamino (e.g. phenoxycarbonylamino); imido (e.g. N-succinimido, N-phthalimido, 3-octadecenylsuccinimido); heterocyclic ring-thio (e.g. 2-benzothiazolylthio, 2,4-diphenyloxy-1,3,5-triazole-6-thio, 2-pyridylthio); sulfinyl (e.g. dodecanesulfinyl, 3-pentadecylphenylsulfinyl, 3-phenoxypropylsulfinyl); phosphonyl (e.g. phenoxyphosphonyl, octyloxyphosphonyl, phenylphosphonyl); aryloxycarbonyl (e.g. phenoxycarbonyl); acyl (e.g. acetyl, 3-phenylpropanoyl, benzoyl, 4-dodecyloxybenzoyl); azolyl (e.g. imidazolyl, pyrazolyl, 3-chloropyrazol-1-yl).

These substituents may be substituted further, for example by halogen or by an organic radical attached via a C, O, N or S atom.

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The preferred groups R₁₁ are alkyl, aryl, alkoxy, aryloxy, alkylthio, ureido, urethane and acylamino groups.

R₁₂ may be as defined for R₁₁ and is preferably hydrogen, alkyl, aryl, a heterocyclic ring, alkoxycarbonyl, carbamoyl, sulfamoyl, sulfinyl, acyl or cyano.



R₁₃ may be as defined for R₁₁ and is preferably hydrogen, alkyl, aryl, heterocyclyl, alkoxy, aryloxy, alkylthio, arylthio, alkoxycarbonyl, carbamoyl or acyl, preferably alkyl, aryl, heterocyclyl, alkylthio or arylthio.

Q is hydrogen or a leaving group such as halogen, alkoxy, aryloxy, acyloxy, alkyl- or arylsulfonyloxy, acylamino, alkyl- or arylsulfonamido, alkoxycarbonyloxy, aryloxycarbonyloxy, alkyl-, aryl- or heterocyclyl-S-carbamoylamino, a 5- or 6-membered nitrogen-containing heterocyclic radical, imido and arylazo. These groups may be further substituted as indicated for R_{11} .

Q is preferably halogen (for example fluorine, chlorine, bromine); alkoxy (e.g. ethoxy,

dodecyloxy, methoxyethylcarbamoylmethoxy, carboxypropyloxy, methylsulfonylethoxy, ethoxycarbonylmethoxy); aryloxy (e.g. 4-methylphenoxy, 4-chlorophenoxy, 4-methoxyphenoxy, 4-carboxyphenoxy, 3-ethoxycarboxyphenoxy, 3-acetylaminophenoxy, 2-carboxyphenoxy); acyloxy (e.g. acetoxy, tetradecanoyloxy, benzoyloxy); alkyl- or arylsulfonyloxy (e.g. methanesulfonyloxy, toluenesulfonyloxy); acylamino (e.g. dichloroacetylamino, heptafluorobutyrylamino); alkyl- or arylsulfonamido (e.g. methanesulfonamido, trifluoromethanesulfonamido, p-toluenesulfonylamido); alkoxycarbonyloxy (e.g. ethoxycarbonyloxy, benzyloxycarbonyloxy); aryloxycarbonyloxy (e.g. phenoxycarbonyloxy); alkyl-, aryl- or heterocyclyl-S- (e.g. dodecylthio, 1-carboxydodecylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, tetrazolylthio); carbamoylamino (e.g. N-methylcarbamoylamino, N-phenylcarbamoylamino); 5- or 6-membered nitrogen-containing ring (e.g. imidazolyl, pyrazolyl, triazolyl, tetrazolyl, 1,2-dihydro-2-oxo-1-pyridyl); imido (e.g. succinimido, hydantoinyl); arylazo (e.g. phenylazo, 4-methoxyphenylazo).

Q may alternatively form corresponding bis-compounds by condensation of 4 equivalents of coupler with an aldehyde or ketone. Furthermore, Q may contain photographically active groups, such as development inhibitors or development accelerators. Q is preferably



halogen, alkoxy, aryloxy, alkyl- or arylthio, or a 5- or 6-membered nitrogen-containing heterocyclic group which is bonded to the coupling site via a nitrogen atom.

Pyrazolotetrazoles are described in JP-A-85/33552; pyrazolopyrazoles in JP-A-85/43,695; pyrazoloimidazoles in JP-A-85/35732, JP-A-86/18949 and US-A-4,500,630; pyrazolotriazoles in JP-A-85/186,567, JP-A-86/47957, JP-A-85/215,687, JP-A-85/197,688, JP-A-85/172,982, EP-A-119,860, EP-A-173,256, EP-A-178,789, EP-A-178,788 and in Research Disclosure 84/24,624.

Further pyrazoloazole magenta couplers are described in: JP-A-86/28,947, JP-A-85/140,241, JP-A-85/262,160, JP-A-85/213,937, JP-A-87/278,552, JP-A-87/279,340, JP-A-88/100,457, EP-A-177,765, EP-A-176,804, EP-A-170,164, EP-A-164,130, EP-A-178,794, DE-A-3,516,996, DE-A-3,508,766 and Research Disclosure 81/20919, 84/24531 and 85/25758.

Suitable examples of such couplers are:

$$(CH_3)_3C$$
 N
 N
 N
 $CH_2-CH_2-CH_2-SO_2-C_{12}H_{25}$
 $(M-5)$

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$$\begin{array}{c|c} CI & H \\ \hline N & N \\ \hline N & N \\ \hline \end{array} \\ \begin{array}{c} (CH_2)_3 \\ \hline \end{array} \\ \begin{array}{c} NHSO_2 \\ \hline \end{array} \\ \begin{array}{c} OC_{12}H_{25} \\ \hline \end{array}$$

$$\begin{array}{c|c} CI & H \\ \hline \\ N & N \\ \hline \\ N & N \\ \hline \\ CH_3 \\ \hline \\ CH_3 \\ \hline \\ CH_3 \\ \hline \\ OC_8H_{17} \\ OC_8$$



$$(i)C_3H_7 \xrightarrow{CI} \stackrel{H}{N} \xrightarrow{N} OC_4H_9$$

$$N \longrightarrow (CH_2)_3SO_2 \longrightarrow (M-12)$$

(M-11)

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$$(i)C_3H_7 \xrightarrow{CI} \overset{H}{\stackrel{N}{\stackrel{}}} \overset{OC_4H_g}{\stackrel{}}$$

$$N \xrightarrow{\qquad \qquad \qquad \qquad } (CH_2)_2NHSO_2 \xrightarrow{\qquad \qquad \qquad } C_8H_{17}(t)$$

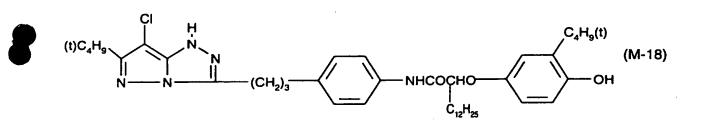
$$(M-14)$$

$$(t)C_{4}H_{9} \xrightarrow{\dot{N}} N \xrightarrow{\dot{N}} N = (CH_{2})_{2}SO_{2}C_{18}H_{37}$$
(M-15)

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$$(t)C_4H_9 \xrightarrow{V} N \qquad OC_4H_9 \qquad OC_4H_9$$

$$(CH_2)_3SO_2 \qquad C_8H_{17}(t)$$



$$(t)C_4H_9 + H_9 + H_9$$

$$C_{2}H_{5}S \downarrow \begin{matrix} H \\ N \end{matrix} C_{8}H_{17}(t) & C_{5}H_{11}(t) \\ N \end{matrix} CH_{2}CH_{2}NHCOCHO - C_{5}H_{11}(t)$$

$$C_{4}H_{9} \qquad (M-20)$$

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$$\begin{array}{c|c} CI & H & OC_8H_{17} \\ \hline CH_3 & CHCH_2NHSO_2 & OC_8H_{17} \\ \hline CH_3 & NHSO_2 & OC_8H_{17} \\ \hline \end{array}$$

$$\begin{array}{c|c} CI & H & OC_8H_{17} \\ \hline CH_3 & OC_8H_{17} \\ \hline \end{array}$$

$$\begin{array}{c|c} CI & H & OC_8H_{17} \\ \hline CH_3 & OC_8H_{17} \\ \hline \end{array}$$

$$\begin{array}{c|c} CI & H & OC_8H_{17} \\ \hline \end{array}$$

$$CH_3 \downarrow \downarrow \downarrow \stackrel{CI}{N} \downarrow \downarrow CHCH_2SO_2 \longrightarrow OC_{12}H_{25}$$

$$CH_3 \downarrow \downarrow \downarrow \stackrel{C}{N} \downarrow CHCH_2SO_2 \longrightarrow OC_{12}H_{25}$$

$$CH_3 \downarrow \downarrow \stackrel{C}{N} \downarrow \stackrel{C}{N} \downarrow CHCH_2SO_2 \longrightarrow OC_{12}H_{25}$$

$$CH_{3} \xrightarrow{V} CH_{2}CH_{2}SO_{2} \xrightarrow{OC_{8}H_{17}} CH_{2}CH_{2}SO_{2} \xrightarrow{OC_{8}H_{17}(t)} (M-24)$$

$$CH_{3} \xrightarrow{V} V CHCH_{2}NHSO_{2} CHCH_{2}NHSO_{2} CHCH_{3}N CHCH_{2}NHSO_{2} CHCH_{3}N CHCH_{3}N$$

(i)
$$C_3H_7$$
 V CH_3 $C-CH_2SO_2C_{18}H_{37}$ (M-26)

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$$(t)C_4H_9 \xrightarrow{N} N \xrightarrow{CH_3} CH_3$$

$$CH_3 \qquad NHCOCHO \longrightarrow SO_2 \longrightarrow OH$$

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$$(t)C_8H_{17}$$

$$CH_3$$

$$CH_3$$

$$N$$

$$N$$

$$CHCH_2NHSO_2$$

$$C_8H_{17}(t)$$

$$C_8H_{17}(t)$$

$$(t)C_8H_{17}$$

$$C_2H_5O$$

$$N$$

$$N$$

$$C_2H_5O$$

$$N$$

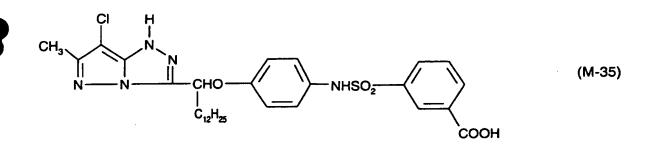
$$C_1H_2NHSO_2$$

$$C_8H_{17}$$

$$C_8H_{17}(t)$$

$$(CH_3)_3C \downarrow \begin{matrix} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\$$

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$$\begin{array}{c|c}
CI & H \\
N & N \\
CH_2CH_2CH_2O
\end{array}$$

$$\begin{array}{c}
C_5H_{11}(t)
\end{array}$$

$$\begin{array}{c}
C_5H_{11}(t)
\end{array}$$

$$(CH_3)_3C \xrightarrow{\qquad \qquad \qquad \qquad \qquad } CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_2 \\ CH_2 \\ C_{12}H_{25} \\ (M-37)$$

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(i)
$$C_3H_7$$
 N
 $CH_2CH_2CH_2SO_2$
 $C_8H_{17}(t)$

(M-39)

$$\begin{array}{c|c} CI & H & OC_8H_{17} \\ \hline \\ (t)C_4H_9 & & \\ \hline \\ N & N & \\ \hline \\ N & N & \\ \end{array}$$

$$\begin{array}{c|c} CHCH_2NHSO_2 & OC_4H_9 \\ \hline \\ C_2H_5 & \\ \hline \\ C_8H_{17}(t) & \\ \end{array}$$

$$\begin{array}{c|c} CG_8H_{17} & OC_4H_9 \\ \hline \\ CG_8H_{17}(t) & \\ \hline \end{array}$$

$$\begin{array}{c|c} CG_8H_{17}(t) & OC_4H_9 \\ \hline \\ CG_8H_{17}(t) & \\ \hline \end{array}$$

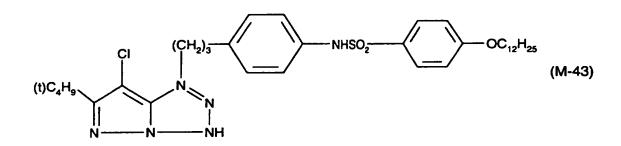
$$(t)C_4H_9 \xrightarrow{CI} \underset{N}{H} CH_2CH_2NHSO_2 \xrightarrow{OC_8H_{17}} (M-41)$$

$$C_8H_{17}(t)$$

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$$(t)C_4H_9 \longrightarrow (CH_2)_3 \longrightarrow (CH_2)_3 \longrightarrow (CH_2)_3 \longrightarrow (CI_1_0H_2)_4 \longrightarrow$$



$$C_{15}H_{31}$$

$$(t)C_{5}H_{11} \longrightarrow OCH_{2} \longrightarrow N \longrightarrow N \longrightarrow C_{13}H_{27}$$

$$(M-45)$$

$$CH_{2} \downarrow \downarrow \downarrow N \qquad N \qquad N \qquad (M-46)$$

$$CI$$

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$$\begin{array}{c|c} CI & H & OC_4H_9 \\ \hline N & N & \\ \hline N & (CH_2)_3SO_2 & \\ \hline & C_8H_{17}(t) \end{array}$$

(i)
$$C_3H_7$$

N

C₅H₁₁(t)

C₅H₁₁(t)

C₆H₁₃

(M-50)

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$$\begin{array}{c|c}
CI & H \\
N & N \\
N & N \\
N & (CH_2)_2 NHSO_2
\end{array}$$

$$\begin{array}{c}
C_8 H_{17}(t)
\end{array}$$

$$\begin{array}{c}
C_8 H_{17}(t)
\end{array}$$

$$CH_3$$
 N
 CH_3
 $CH_$

$$(t)C_4H_9 \xrightarrow{\qquad \qquad \qquad \qquad \qquad } CH_3$$

$$CH_3 \qquad \qquad C_5H_{11}(t)$$

$$CH_3 \qquad \qquad \qquad \\ CH_3 \qquad \qquad \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \\ CH_3 \qquad \qquad \\ CH_3 \qquad \qquad \\ CH_4 \qquad \qquad \\ CH_5 \qquad \qquad \\ CH_5 \qquad \qquad \\ CH_5 \qquad \\ CH_5 \qquad \\ CH_5 \qquad \\ CH_5 \qquad \\ CH_5 \qquad \\ CH_5 \qquad \\ CH_5 \qquad \qquad \\ CH_5$$

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$$(t)C_4H_9 \downarrow I \qquad C_5H_{11}(t) \qquad (M-57)$$

$$N \downarrow N \qquad C_5H_{11}(t) \qquad (M-57)$$

$$C_5H_{11}(t) \qquad C_5H_{11}(t)$$

$$CH_{3} \xrightarrow{II} N$$

$$N$$

$$CH-CH_{2}NH-SO_{2} \xrightarrow{OC_{8}H_{17}}$$

$$CH_{3}$$

$$NHSO_{2} \xrightarrow{C_{8}H_{17}(t)}$$

$$C_{8}H_{17}(t)$$

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$$CH_{3} = N - N - N - N - CH_{3} - C_{5}H_{11}(t)$$

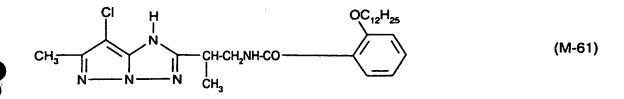
$$CH_{3} = C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$



$$CH_3 \longrightarrow N \longrightarrow N \longrightarrow N \longrightarrow CH_3$$

$$CH_2NH-CO(CH_2)_3O \longrightarrow C_5H_{11}(t)$$

$$C_5H_{11}(t) \longrightarrow C_5H_{11}(t)$$

$$C_5H_{11}(t) \longrightarrow C_5H_{11}(t)$$

$$CH_{3} \downarrow \downarrow N \qquad CHCH_{2}NH-COCHO \qquad C_{10}H_{21} \qquad (M-63)$$

$$CH_{3} \downarrow C_{10}H_{21} \qquad C_{15}H_{31}$$

$$CH_{3} \longrightarrow N \longrightarrow N \qquad CHCH_{2}NHCOCH-O \longrightarrow CH_{3} \qquad C_{6}H_{13} \qquad OC_{12}H_{25} \qquad (M-64)$$

$$(i)C_{3}H_{7} \xrightarrow{|C|} N \xrightarrow{|C|} C_{5}H_{11}(t) \xrightarrow{|C|} C_{5}H_{11}(t) \xrightarrow{|C|} C_{5}H_{11}(t) \xrightarrow{|C|} C_{5}H_{11}(t) \xrightarrow{|C|} C_{5}H_{11}(t)$$



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$$CH_{3} = N - N - N - N - CH_{3} - CH_{11}(t) - CH_{2}(CH_{2})_{4}NH-CO-CH-O - C_{5}H_{11}(t) - C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t) - C_{5}H_{11}(t)$$

$$C_{6}H_{13} - C_{6}H_{13}(t) - C_{5}H_{11}(t)$$

$$(t)C_4H_9 \longrightarrow N \longrightarrow N \longrightarrow N \longrightarrow CH_2NH-CO-CH-O \longrightarrow C_5H_{11}(t)$$

$$(M-67)$$

$$C_5H_{11}(t)$$

$$C_5H_{11}(t)$$

Cyan couplers can, for example, be derivatives of phenol, 1-naphthol, pyrazoloazole, pyrroloazole or of pyrazoloquinazolone. One group of cyan couplers is of the formula E

in which R_{21} , R_{22} , R_{23} and R_{24} are hydrogen, halogen, alkyl, carbamoyl, amino, sulfonamido, phosphoramido or ureido. R_{21} is preferably H or Cl, R_{22} is preferably an alkyl or amino group. R_{23} is preferably an amino group and R_{24} is preferably hydrogen. Q" is hydrogen (4-equivalent coupler) or a leaving group (2-equivalent coupler) which is eliminated on reaction with the oxidized developer. An exhaustive listing of cyan couplers can be found in US-A-4,456,681.

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The cyan couplers employed in the red-sensitive silver halide emulsion layer of the novel material are preferably of the formula

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and/or of the formula

(E-13) CI NHCOZ₅
$$Z_7$$
 Z_8

in which

 Z_1 is alkyl, aryl, Z_2 is alkyl, cycloalkyl, aryl, a heterocyclic group or a ballast group, Z_3 is hydrogen or halogen, Z_1 and Z_3 together can form a ring, and Z_4 is hydrogen or a leaving group, and Z_5 is a ballast group, Z_6 is hydrogen or a leaving group and Z_7 is alkyl



and/or also those of the formulae E20 and E21

in which R_1 is preferably substituted phenyl and R_2 and R_3 are preferably H and X is preferably H or a group which is cleaved by reaction with the oxidized form of the developer, and

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in which Za is -NH- or -CH(R₃)-; Zb and Zc independently of one another are -C(R₄)= or -N=; R₁, R₂ and R₃ are each an electron-attracting group having a Hammett substituent constant σ_p of at least 0.2, with the sum of the σ_p values of R₁ and R₂ being at least 0.65; R₄ is H or a substituent, and if two R₄s are present in the formula, they can be identical or different; and X is H or a group capable of elimination in the coupling reaction with the oxidation product of an aromatic primary amine as colour developer; or R₁, R₂, R₃, R₄ or X is a divalent group by means of which the cyan coupler is able to form a dimer or higher polymer, or to react with a polymer chain to form a homo- or copolymer.

Preference is given to a photographic material in which the red-sensitive silver halide emulsion layer comprises a cyan coupler of one of the formulae C1, C2, C3, C4, C5, C6, C7 and C8

$$Z_3$$
 NH-CO- Z_2 C1 Z_1 CO-NH Z_4

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$$Z_{B}$$
 Z_{B}
 Z_{B

СЗ

$$Z_{B} \downarrow V \downarrow N \downarrow N \downarrow X_{11} \downarrow X_{11} \downarrow X_{12} \downarrow X_{13} \downarrow X_{14} \downarrow X_{15} \downarrow$$

C4

$$Z_{8}$$
 Z_{9}
 N
 N
 N
 N
 N
 N
 N

C5

$$Z_{8} \downarrow \downarrow X_{10} \downarrow$$

C6



C7

C8

in which

Z₁ is alkyl or aryl,

 Z_2 is alkyl, cycloalkyl, aryl, a heterocyclic group or a ballast group,

 Z_3 is H or halogen, or Z_1 and Z_3 together form a ring,

Z₄ is H or a leaving group,

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Z₅ is a ballast group,

Z₆ is H or a leaving group,

Z₇ is alkyl,

 Z_8 and Z_9 independently of one another are H or a substituent, at least one of the groups Z_8 and Z_9 being an electron-withdrawing group having a Hammett constant $(-\sigma_p)$ of 0.15 or more $[Z_8]$ and Z_9 can be connected to one another to form a ring structure];

Z₁₀ is a substituent and

Z₁₁ is H or a leaving group.

The cyan couplers can also be connected to one another by way of the radicals Z_8 , Z_9 , Z_{10} or Z_{11} to form dimers or polymers.

Suitable leaving groups are in general those substituents which are set free after coupling with the oxidation product of a colour developer based on aromatic primary amines.

The novel photographic material preferably comprises those cyan couplers of the formulae C1-C8 in which

Z₁ is alkyl or aryl,

Z₂ is alkyl, aryl, or a ballast group,

Z₃ is H or halogen,

Z₄ is H or a leaving group,

Z₅ is a ballast group,

Z₆ is H or a leaving group,

Z₇ is alkyl,

 Z_8 and Z_9 independently of one another are CN, CF₃, COOZ₁₂, COZ₁₂, SO₂Z₁₂, CON(Z₁₃)Z₁₄,

SO₂N(Z₁₃)Z₁₄, and

Z₁₂ is unsubstituted alkyl or aryl,

 Z_{13} and Z_{14} independently of one another are unsubstituted or substituted alkyl, aryl, heterocyclyl, alkoxy, aryloxy or heterocyclyloxy, and

Z₁₃ can also be H;

 Z_{10} embraces the definitions given for Z_8 and Z_9 or is alkyl, aryl, heterocyclyl, nitro, NH-CO-

 $Z_{15},\ N(Z_{15})Z_{16},\ NH-CO-N(Z_{15})Z_{16},\ NH-SO_2N(Z_{15}),\ S-Z_{15},\ NH-CO-OZ_{15},\ NH-SO_2N(Z_{15})Z_{16},\ NH-SO_2N(Z_{15})Z_{16}$

SOZ₁₅, and

Z₁₅ and Z₁₆ are each a substituent, and Z₁₆ can also be H.

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The colour developers usually used for colour photographic recording materials are p-dialkylaminoanilines. Examples of these are 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N- α -hydroxyethylaniline,

3-methyl-4-amino-N-ethyl-N-α-hydroxyethylaniline,

3-methyl-4-amino-N-ethyl-N- α -hydroxyethylaniline,

3-methyl-4-amino-N-ethyl-N-α-methanesulfonamidoethylaniline,

3-methyl-4-amino-N-ethyl-N-α-methoxyethyl-aniline,

3-α-methanesulfonamidoethyl-4-amino-N,N-diethylaniline,

3-methoxy-4-amino-N-ethyl-N-α-hydroxyethylaniline,

3-methoxy-4-amino-N-ethyl-N-α-methoxyethylaniline,

3-acetamido-4-amino-N,N-diethylaniline, 4-amino-N,N-dimethylaniline,

N-ethyl-N- α -[α '-(α "-methoxyethoxy)ethoxy]ethyl-3-methyl-4-aminoaniline,

N-ethyl-N- α -(α '-methoxyethoxy)ethyl-3-methyl-4-aminoaniline, and also the salts of such compounds, for example sulfates, hydrochlorides or toluenesulfonates.

The compounds of the formula (I) which can be used in the context of this invention can be incorporated into the colour photographic recording material, on their own or together with the colour coupler and with or without further additives, by predissolving them in high-boiling organic solvents. Preference is given to the use of solvents which boil at higher than 160°C. Typical examples of these solvents are the esters of phthalic acid, phosphoric acid, citric acid, benzoic acid or of fatty acids, and also alkylamides and phenols.



A low-boiling solvent is usually used in addition in order to simplify incorporation of the additives into the colour-photographic recording material. Examples of such solvents are esters, for example ethyl acetate, alcohols, for example butanol, ketones, for example methyl isobutyl ketone, chlorinated hydrocarbons, such as methylene chloride, and amides, such as dimethylformamide. Where the additives themselves are liquid, they can also be incorporated into the photographic material without the assistance of solvents.

The novel compounds of the formula (I) may if desired be dispersed in the gelatine layer without oil, as described Research Disclosure, Items 296017 (1988) and 303070 (1989).

The photographic layers in the material of this invention may also include UV absorbers, which screen out the UV light and therefore protect the dyes, the couplers or other

components against photodegradation. Benzofuran-2-ones compounds according to this invention may be contained in those layers where UV absorbers are present.

UV absorbers preferably to be used in the novel material or within the process of present invention include benzotriazoles, 2-hydroxybenzophenones, oxanilides, cyanoacrylates, salicylic esters, acrylonitrile derivatives, thiazolines and 2-hydroxyphenyltriazines.

Such UV absorbers are described in more detail, for example, in the following publications: DE 19750906, US-A-3,314,794, 3,352,681, 3,705,805, 3,707,375, 4,045,229, 3,700,455, 3,700,458, 3,533,794, 3,698,907, 3,705,805, 3,738,837, 3,762,272, 4,163,671, 4,195,999, 4,309,500, 4,431,726, 4,443,543, 4,576,908, 4,749,643, 4,826,978, 5,500,332, 5,455,152, 5,300,414, 5,489,503, 5,480,108, 5,364,749, GB-A-1,564,089, GB-A-2,293,608, EP-A-190003, -747755, -717313 and JP-A-71/2784, 81/111,826, 81/27,146, 88/53,543, 88/55,542 and 96/69087.

Examples of particularly suitable UV absorbers are:

2-Hydroxyphenyltriazines of the formula

$$G_1O$$
 G_2
 G_3
 G_4

in which j is 0, 1, 2 or 3;

G, is alkyl, alkenyl or cycloalkyl;

 G_2 and G_6 independently of one another are H, OH, halogen, alkyl, alkoxy, halomethyl, for example CF_3 ;

G₃, G₅ and G₇ independently of one another are H, OH, OG₁, halogen, alkyl, halomethyl, for example CF₃;

 G_4 is H, OH, OG₁, halogen, alkyl, phenyl, halomethyl, for example CF₃, or alkenyl; and G_{12} is alkyl, phenylalkyl, cycloalkyl, OG₁, or in particular, a group of the formula

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$$G_2$$
 G_3
 G_4

Alkyl or alkenyl substituents, or substituents which are aromatic or aliphatic ring systems, usually contain - within the context of the stated definitions - from 1 to 50 carbon atoms and can be interrupted one or more times by O, S, NR', SO₂, CO, phenylene, cyclohexylene, COO, OCO, -(SiR_pR_qO)- and/or substituted one or more times by OH, OR', NR'R", halogen, - CN, alkenyl, phenyl, -SiR_pR_qR_r or COOH, where R' and R" independently of one another are H, alkyl, alkenyl or acyl, and R_p, R_q and R_r independently of one another are H, alkyl, alkenyl, alkoxy, acyl or acyloxy.

The abovementioned groups can also carry other substituents as well. Dimers or polymers are also possible.

Preferred 2-hydroxyphenyltriazines of this class are, for example, those of the formula

$$G_{3}$$

$$G_{2}$$

$$G_{1}$$

$$G_{2}$$

$$G'_{3}$$

$$G'_{3}$$

$$G'_{3}$$

$$G'_{4}$$

$$G$$

$$G'_{2}$$

$$G'_{4}$$

or

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$$R_{101}$$
 R_{102}
 R_{103}
 R_{103}
 R_{103}
 R_{103}
 R_{103}
 R_{103}

where, in formula AIII

n is 1 or 2 and

R'. R9

 G_1 , if n = 1, is alkyl which is uninterrupted and unsubstituted or is interrupted by one or more O and/or substituted by one or more of the radicals OH, glycidyloxy, alkenoxy, COOH, COOR⁶, O-CO-R^f, or is alkenyl, cycloalkyl, unsubstituted or OH-, CI- or CH₃-substituted phenylalkyl; or COR⁹; SO_2 -R^h; $CH_2CH(OH)$ -Rⁱ; where

R^e is alkyl; alkenyl; hydroxyalkyl; alkyl or hydroxyalkyl interrupted by one or more O; cycloalkyl; benzyl; alkylphenyl; phenyl; phenylalkyl; furfuryl; or CH₂CH(OH)-Rⁱ;

independently of one another are alkyl, alkenyl or phenyl;

R^h is alkyl, aryl or alkylaryl;

R^j is aralkyl or CH₂OR^k;

R^k is cyclohexyl, phenyl, tolyl or benzyl; and

 G_1 , if n = 2, is alkylene; alkenylene; xylylene; alkylene or hydroxyalkylene interrupted by one or more O; hydroxyalkylene;

G₂ and G'₂ independently of one another are H, alkyl, alkoxy or OH;

 G_4 and G'_4 independently of one another are H, alkyl, OH, alkoxy, halogen, and, if n = 1, OG_1 :

 G_3 and G_3 independently of one another are H, alkyl or halogen; and where, in formula AV,

R₁₀₁ is H, C₁-C₈alkyl, C₁-C₈alkoxy;

 R_{102} and R_{103} independently of one another are H, halogen, OH, C_1 - C_8 alkyl, C_1 - C_8 alkoxy;

R₁₀₄ is H, OH, C₁-C₈alkyl; C₁-C₈alkoxy.

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Within the scope of the stated definitions G₁, G₂, G'₂, G₃, G'₃, G₄ and G'₄ may also carry additional substituents, for example an ethylenically unsaturated, polymerizable group. Dimers or polymers are also possible.

Particular preference is given to colour photographic materials in accordance with the present invention, in which at least one of the layers comprises a UV absorber of the formula A III in which

n is 1:



 G_1 is C_1 - C_{12} alkyl which is unsubstituted or substituted by OH or COOR $^{\circ}$; or is C_2 - C_{12} alkyl or C_3 - C_{15} hydroxyalkyl, interrupted by one or more O; or is C_3 - C_6 alkenyl; cyclohexyl; C_7 -

C₁₁phenylalkyl; CH₂CH(OH)-Rⁱ; where

R° is C₁-C₁₈alkyl; C₃-C₇alkenyl; alkyl or hydroxyalkyl interrupted by one or more O;

Rⁱ is C₇-C₁₂aralkyl or CH₂OR^k;

R^k is cyclohexyl, phenyl, tolyl or benzyl; and

G₂ and G'₂ are OH or alkoxy;

G₄ and G'₄ are OG₁;

G₃ and G'₃ independently of one another are H or methyl;

especially those in which

n is 1:

G₁ is C₁-C₁₂alkyl which is unsubstituted or substituted by COOR^e; or is C₃-C₁₅hydroxyalkyl which is interrupted by O; or is allyl, cyclohexyl or benzyl; where



R^e is C₁-C₁₂alkyl; allyl; C₃-C₁₂alkyl which is interrupted by one or more O;

G₂ and G'₂ are OH or alkoxy;

G₄ and G'₄ are OG₁;

G₃ and G'₃ are H.

Examples of such compounds include

2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine,

2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine,

2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine,

2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

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j

2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,

2-[2-hydroxy-4-(2-hydroxy-3-tridecyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; and compounds of the following formulae:

Type (HPT-I)
$$G_3$$

$$G_1$$

$$G_2$$

$$G_3$$

$$G_2$$

$$G_3$$

$$G_2$$

$$G_3$$

| No. | G ₁ | G ₂ | G₄ | G ₃ |
|-------|---|-----------------|-----------------|----------------|
| HPT-1 | CH₂CH(OH)CH₂O-CO-C(CH₃)=CH₂ | CH ₃ | CH ₃ | Н |
| HPT-2 | CH ₂ CH(OH)CH ₂ OC ₁₂ H ₂₅ /C ₁₃ H ₂₇ (mixture) | CH₃ | CH₃ | Н |
| HPT-3 | CH₂CH(OH)CH₂O-C₄H₃(n) | CH₃ | CH₃ | Н |
| HPT-4 | CH ₂ COO-C ₁₈ H ₃₇ | Н | н | m-CF₃ |
| HPT-5 | C ₈ H ₁₇ | CH₃ | CH₃ | Н |
| HPT-6 | CH ₂ CH(OH)CH(C ₂ H ₅)-C ₄ H ₉ (n) | CH ₃ | CH ₃ | Н |
| HPT-7 | н | CH₃ | CH₃ | Н |
| HPT-8 | CH₂CH₂OH | Н | Н | Н |
| HPT-9 | C ₈ H ₁₇ | Н | Н | Н |

Type (HPT-II)
$$G_1O \qquad \qquad G_2 \qquad G_3 \qquad \qquad G_4$$

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| No. | G ₁ | G₂ | G₄ | G ₃ |
|----------|--|------------------|---------------------------------|-------------------|
| HPT-10 | C ₁₈ H ₃₇ | CH₃ | CH₃ | o-CH₃ |
| HPT-11 | CH₂CH(OH)CH₂O-C₄H₃(n) | Н | Н | Н |
| HPT-12 | CH₂CH(OH)CH₂O-C₄H₃(n) | CH₃ | CH₃ | Н |
| HPT-13 | CH₂CH(OH)CH₂O-C₄H₃(n) | CH₃ | CH₃ | o-CH₃ |
| HPT-14 | CH₂CH(OH)-C₄H₃(n) | CH₃ | CH ₃ | o-CH₃ |
| HPT-15 | CH(OH)-C₅H₁₁(n) | CH₃ | CH ₃ | o-CH ₃ |
| HPT-16 | C _B H ₁₇ | Н | CI | Н |
| HPT-17 | CH(CH₃)-COO-C₂H₅ | CH ₃ | CH₃ | o-CH ₃ |
| HPT-18 | $CH_2CH(OCOCH_3)CH(C_2H_5)-C_4H_9(n)$ | Н | Н | Н |
| HPT-19 | CH₂CH(OH)CH(C₂H₅)-C₄H₅(⊓) | Н | Н | Н |
| HPT-20 | CH ₂ CH ₂ -O-CO-C(CH ₃) ₃ | Н | Н | Н |
| HPT-21 | H | Н | Н | Н |
| HPT-22 | (CH ₂) ₁₀ COO-C ₂ H ₅ | Н | CI | Н |
| HPT-23 | (CH₂)₅COOH | Н | Н | Н |
| HPT-24 | CH ₂ CH(C ₂ H ₅)-C ₄ H ₉ (n) | Н | Н | Н |
| HPT-25 | CH ₂ CH(OH)CH ₂ -O-C ₄ H ₉ (n) | Н | t-C ₄ H ₉ | Н |
| HPT-26 | CH ₂ CH(OH)CH ₂ -O-C ₄ H ₉ (n) | Н | OCH ₃ | Н |
| HPT-27 | (CH ₂) ₃ -Si(CH ₃) ₃ | Н | Н | Н |
| HPT-28 | CH ₂ -CH(OH)-CH ₂ -O-C ₄ H ₉ -n | OCH ₃ | OG ₁ | Н |
| HPT-29 | CH₂-CH(OH)-CH₂-O-C₄H₃-n | OC₂H₅ | OG ₁ | н |
| . HPT-30 | CH₂-CH(OH)-CH₂-O-C₄H₃-n | OG ₁ | OG ₁ | н |
| HPT-31 | CH(CH₃)-CO-O-C₂H₅ | OC₂H₅ | OG ₁ | Н |
| HPT-32 | CH(CH₃)-CO-O-C₂H₅ | OG ₁ | OG ₁ | Н |
| HPT-33 | · /= | OCH ₃ | OG ₁ | Н |
| | _nC | | | |
| | 1 | | | |
| | (mixture of 4-vinyl- and 5-vinyl-2- | | | |
| | hydroxy-cyclohexyl) | | | |
| HPT-34 | C₂H₅ | OG ₁ | OG ₁ | Н |
| HPT-35 | CH₂-CH(C₂H₅)-C₄H ₉ -n | OG ₁ | OG ₁ | Н |
| HPT-36 | (CH ₂) ₇ -CH ₃ | OG ₁ | OG ₁ | н |
| HPT-37 | n-propyl | OCH₃ | OG_1 | Н |
| HPT-38 | n-propyl | O C₂H₅ | OG ₁ | Н |

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| HPT-39 | n-propyl | OG ₁ | OG ₁ | Н |
|--------|----------------|--------------------------------|-----------------|---|
| HPT-40 | iso-propyl | OCH₃ | OG ₁ | Н |
| HPT-41 | iso-propyl | OC₂H₅ | OG ₁ | Н |
| HPT-42 | iso-propyl | OG ₁ | OG ₁ | Н |
| HPT-43 | n-butyl | OCH₃ | OG, | Н |
| HPT-44 | n-butyl | OC ₂ H ₅ | OG ₁ | Н |
| HPT-45 | n-butyl | OG ₁ | OG ₁ | Н |
| HPT-46 | CH(CH₃)C₂H₅ | OCH₃ | OG ₁ | Н |
| HPT-47 | CH(CH₃)C₂H₅ | OC ₂ H ₅ | OG ₁ | Н |
| HPT-48 | CH(CH₃)C₂H₅ | OG ₁ | OG ₁ | Н |
| HPT-49 | n-hexyl | OCH₃ | OG ₁ | Н |
| HPT-50 | n-hexyl | OC ₂ H ₅ | OG ₁ | Н |
| HPT-51 | п-hexyl | OG ₁ | OG ₁ | Н |
| HPT-52 | n-octyl | OCH₃ | OG ₁ | Н |
| HPT-53 | n-octyl | OC ₂ H ₅ | OG ₁ | H |
| HPT-54 | n-octyl | OG ₁ | OG ₁ | Н |
| HPT-55 | CH₂CH(CH₃)₂ | OG ₁ | OG ₁ | Н |
| HPT-56 | CH₂CH₂CH(CH₃)₂ | OG ₁ | OG ₁ | Н |
| HPT-57 | CH2-COO-Et | OC₂H₅ | OG ₁ | Н |
| HPT-58 | CH2-COO-Et | OG ₁ | OG ₁ | Н |

No.

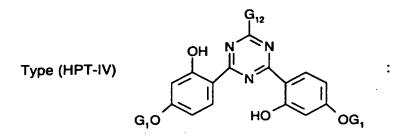
G₁

HPT-59

cyclohexyl

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| HPT-60 | OH (mixture of 4-vinyl- and 5-vinyl-2-hydroxy-cyclohexyl) |
|--------|---|
| HPT-61 | CH₂CH(OH)CH₂-O-2-butyl/2-pentyl (mixture) |
| HPT-62 | CH₂CH(OH)CH₂-O-C₄H ₉ (n) |
| HPT-63 | (CH ₂) ₁₀ COO-C ₂ H ₅ |
| HPT-64 | CH₂CH(OH)CH(C₂H₅)-C₄H₅(n) |
| HPT-65 | C ₄ H ₉ |
| HPT-66 | CH₂CH(OH)CH₂-O-ethyl/isopropyl/C₄H ₉ (n) (mixture) |
| HPT-67 | CH(C₃H ₇)₂ |
| HPT-68 | cyclopentyl |
| HPT-69 | CH₂CH(OH)CH₂-O-CH₂CH₂-O-CH(CH₃)C₂H₅ |
| HPT-70 | OH C |
| HPT-71 | H ₃ C O |
| HPT-72 | C(CH ₃) ₂ -COO-C ₂ H ₅ |
| HPT-73 | CH(CH ₃)-COO-C₂H ₅ |
| HPT-74 | CH₂CH(OH)CH₂-O-CH(CH₃)-C₂H₅/C₃H7 |
| HPT-75 | (CH₂)₅-CH₃ |



| No. | G ₁ | G ₁₂ |
|--------|-------------------------------|------------------|
| HPT-76 | CH₃ | |
| HPT-77 | CH₂CH(OCOCH₃)CH(C₂H₅)-C₄H₃(⊓) | OCH₃ |
| HPT-78 | CH₂CH₂CH₂-O-CO-C₂H₅ | OCH ₃ |

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HPT-79

 $CH_2CH(OH)CH_2-O-C_4H_9(n)$

CH₃

HPT-80

HPT-81

 $CH_2CH(OH)CH_2-O-C_4H_9(n)$

OCH₃

and

НО

| No. | R ₁₀₁ | R ₁₀₂ | R ₁₀₃ | R ₁₀₄ |
|--------|------------------|------------------|------------------|------------------|
| HPT-83 | н | Н | Н | н |

| HPT-84 | Н | CH₃ | CH₃ | Н |
|--------|-----|------------------|------|-----|
| HPT-85 | Н | ОН | Н | Н |
| HPT-86 | н | ОН | Н | CH₃ |
| HPT-87 | Н | OCH ₃ | OCH₃ | Н |
| HPT-88 | CH₃ | Н | Н | Н |

Abbreviations used in above formulae:

i = isomer mixture; n = straight-chain radical; t = tertiary radical; o-, m- and p- denote the position of the radical relative to the triazine ring.

Benzotriazole compounds of the formula All

$$T_3 \longrightarrow N \longrightarrow T_1 \longrightarrow T_4 \longrightarrow$$

in which T_1 and T_2 independently of one another are hydrogen, halogen, alkyl, alkyl substituted by COOT₅, alkoxy, aryloxy, hydroxyl, aralkyl, aryl or acyloxy, where T_5 is alkyl or alkyl interrupted by one or more O,

or T₁ is a group of the formula

in which L₁ is a bivalent

group, for example -(CH₂)_n- where n is from the range 1-8,

 T_3 is hydrogen, halogen, alkyl, alkoxy, aryloxy, acyloxy; -CF₃, phenyl, -S-T₆, -SO₂-T₆; and T_4 is hydrogen, hydroxyl, alkoxy, aryloxy or acyloxy or a group of one of the formulae - OCH₂CH(OT₈)-CH₂-O-T₇ or -OCH₂CH₂-O-CO-T₇;

T₆ is alkyl or aryl;

T7 is alkyl or aryl;

T₈ is hydrogen or CO-T₉;

T₉ is alkyl or alkenyl;

and polymers prepared using these compounds. Preference is given to those compounds of the formula A II which are liquid in the temperature range around 20°C or form a liquid phase in a mixture with other substances, especially to those in which

 T_1 and T_2 independently of one another are hydrogen, halogen, alkyl, alkyl substituted by COOT₅, alkoxy, aryloxy, hydroxyl, aralkyl, aryl or acyloxy, where T_5 is alkyl or alkyl which is interrupted by one or more O.

Within the scope of the stated definitions T_1 , T_2 , T_3 and T_4 may also carry additional substituents, for example an ethylenically unsaturated, polymerizable group. Dimers or polymers are also possible.

Especial preference is given to those compounds of the formula AII, in which

T₁ is H, C₁-C₁₂alkyl, 1,1-dimethylbenzyl;

T₂ is H, C₁-C₁₂alkyl, 1,1-dimethylbenzyl or CH₂CH₂COOT₅;

T₃ is chlorine, CF₃, -S-T₆, -SO₂-T₆;

T₄ is hydrogen or C₁-C₁₈alkoxy;

T₅ is C₁-C₁₈alkyl, or C₃-C₁₈alkyl interrupted by one or more O; and

T₆ is phenyl.

The radicals designated as alkyl, alkenyl, aryl, arylalkyl, acyl, alkyloxy, alkenyloxy, aryloxy, arylalkyloxy and acyloxy for the conventional UV absorbers are generally those which are common in the art; preferred radicals are generally - as regards chain length, number of carbon atoms and any heteroatoms etc. - of the type as defined above for the novel compounds of the formula (I).

Examples of benzotriazoles (HBT) of the formula All are:

$$T_3$$

$$N$$

$$N$$

$$T_2$$

$$T_4$$



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| HBT-No. | T ₁ | T ₂ | T ₃ | T ₄ |
|---------|--|---|----------------|---|
| HBT-1 | Н | CH₃ | Н | Н |
| HBT-2 | Н | C(CH ₃) ₃ | Н | Н |
| НВТ-3 | C(CH ₃) ₃ | CH₃ | CI | Н |
| HBT-4 | C(CH ₃) ₃ | $C(CH_3)_3$ | CI | Н |
| HBT-5 | $C(CH_3)_2C_2H_5$ | C(CH ₃) ₂ C ₂ H ₅ | Н | Н |
| HBT-6 | CH(CH₃)C₂H₅ | C(CH ₃) ₃ | Н | Н |
| НВТ-7 | C(CH ₂) ₂ — | C(CH ₃) ₂ — | н | н |
| HBT-8 | C(CH ₃) ₃ | CH ₂ CH ₂ COOC ₈ H ₁₇ (isomers) | CI | H |
| нвт-9 | C(CH ₃) ₃ | CH ₂ CH ₂ COOC ₈ H ₁₇ (isomers) | Н | Н |
| HBT-10 | C ₁₂ H ₂₅ (isomers) | CH₃ | Н | н |
| HBT-11 | C(CH ₂) ₂ — | -C(CH ₃) ₂ -C(CH ₃) ₃ | Н | н |
| HBT-12 | Н | Н | Н | $O(CH_2)_2$ -O-CO-C(CH_3)= CH_2 |
| HBT-13 | н | H | CI | OCOCH ₃ CH ₂ |
| HBT-14 | н | н | Н | $O \bigcap_{OH} O \bigcap_{C_2H_5}^{C_4H_9(n)}$ |
| HBT-15 | sec-C ₄ H ₉ | sec-C ₄ H ₉ | CI | н |

main product

Other suitable UV absorbers are those of the formula AVI, AVII and AVIII

$$R_1$$
N-CH=CH-CH=C
 R_3
 R_4
(AVI)

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in which

$$R_1$$
, $R_2 = -C_6H_{13}(n)$; R_3 , $R_4 = -CN$

$$R_1, R_2 = -C_2H_5; R_3 = -SO_2$$
 ; $R_4 = -CO-OC_8H_{17}$

$$R_1$$
, $R_2 = -C_2H_5$; $R_3 = -SO_2$; $R_4 = -COO-C_{12}H_{25}$

$$R_1$$
, $R_2 = -CH_2 = CH - CH_2$; R_3 , $R_4 = -CN$

$$R_1$$
 R_2
 $CH-CH=C$
 R_3
 R_4
(AVII)

 R_1 , $R_2 = H$; $R_3 = -CN$; $R_4 = -CO-NHC_{12}H_{25}$

 R_1 , $R_2 = -CH_3$; $R_3 = -CN$; $R_4 = -CO-NHC_{12}H_{25}$

$$CH_3O \longrightarrow CH = C \xrightarrow{CN} (AVIII)$$

Other substances which can be used as light or dark stabilizers are described in US-A-5,580,710 or US-A-5,543,276.

Examples of particularly suited stabilizers for the colour couplers and resulting dyes which can be employed in the novel material are:

(ST-1)

(ST-2)

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(ST-3)

(ST-4)
$$C_3H_7O$$
 C_3H_7O C_3H_7O

(ST-5)

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(ST-10)
$$(t)C_4H_9 \xrightarrow{OH} CH_2 \xrightarrow{CH_2} C_4H_9(t)$$

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(ST-12)
$$HO \longrightarrow CH_2CH_2COO \longrightarrow S$$

(ST-14)
$$\begin{bmatrix} C_4H_9(t) \\ HO - CH_2 \\ C_4H_9(t) \end{bmatrix}_2 C - \begin{bmatrix} CH_3 & CH_3 \\ N-CO-CH=CH_2 \\ CH_3 & CH_3 \end{bmatrix}_2$$

(ST-15) $C_4H_9(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$

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(ST-17)
$$\begin{array}{c} \text{HO} \\ \text{H}_{3}\text{C} \\ \text{O} \\ \text{H}_{3}\text{C} \\ \text{CH}_{3} \\ \text{OH} \end{array}$$

(ST-19)
$$OC_4H_9$$
 $N(C_4H_9)_2$ C_8H_{17}

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(ST-21)

$$O_2S$$
 N
 O_2S
 O_2

(ST-22)

(ST-23)

$$(i)H_{27}C_{13} \\ CH \\ N \\ CH_{23}C_{11} \\ CH_{23}C_{11} \\ CH_{23}(i)$$

(ST-24)

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(ST-25)

(ST-26)

(ST-27)

(ST-28)

(ST 29)

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The compounds of formula I may be used in combination with any known Dox scavengers such as hydrazines, hydrazides, hydroquinones of e.g. formula A-1 or A-2, 6-hydroxychromans of e.g formula A-3 or hydroxylamines of e.g. formula A-4:

A-2

As silver halide emulsions it is possible to use customary silver chloride, silver bromide or silver iodide emulsions or mixtures thereof, such as silver chlorobromide and silver chloroiodide emulsions, in which the silver halides may have all known crystal forms. The use of silver chloride emulsions is accorded particular importance in the material of this novel process. The preparation of such emulsions and their sensitization are described in research disclosure, Item 307105, November 1989.

The silver halide emulsion which can be used to implement this invention can be sensitized for all desired wavelengths, with the aid of sensitizing dyes. Dyes which can be used for this



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purpose are cyanine dyes, merocyanine dyes, holopolar dyes, hemicyanine dyes, styryl dyes or hemioxonol dyes.

The photosensitive material may include water-soluble filter and antihalation dyes. Dyes which can be used for this purpose are oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, anthraquinone dyes and azo dyes.

Further details on the structure of the colour photographic material of the invention, and the components or further additives which can be employed in the novel material, can be found, inter alia, in US-A-5,538,840, column 27, line 25, to column 106, line 16, and in US-A-5,780,625, column 12, line 6, until column 57, line 6, and the publications cited in these 2 references; these passages of US-A-5,538,840 and US-A-5,780,625 are hereby incorporated by reference. Other useful information, how compounds of the formula I can be used in photographic material, can be taken from DE-A-19749083, page 16, line 35, until page 17, line 45, especially the references cited therein. Further important components, especially couplers, are described in US-5,578,437; GB-A-2319523 describes from page 49, line 21, until page 73, line 2, further details of the colour photographic material, especially couplers (page 52, line 1, until page 56, line 22), UV absorbers (page 56, line 25, until page 68, line 1) and dark stabilisers (page 68, line 2, until page 73, line 2).

Besides their use in color photographic materials, compounds of formula (I) also find utility in other recording materials, such as digital recording materials. By such materials are meant, for example, those described in Research Disclosure, Item 31429, 1990.

The invention therefore additionally pertains to non silver halide recording material comprising at least one compound of the formula (I). The novel recording materials comprise, for example, those for pressure-sensitive copying systems, microcapsule photocopier systems, heat-sensitive copier systems and ink-jet printing.

The recording materials according to this invention containing a compound of formula (I) feature an unexpectedly high quality, especially in terms of their light and dark stability.

The novel recording materials have a structure which is known per se and which corresponds to the utility. They consist of a base, for example paper or plastic film, on which one or more coatings are applied. Depending on the type of material, these coats contain the suitable components required. The material intended especially for ink-jet printing has a

customary base on which there is an absorption layer suitable for ink. Uncoated paper can likewise be employed for ink-jet printing; in this case, the paper functions simultaneously as a base and has the absorbent for the ink. Suitable material for ink-jet printing is described, inter alia, in U.S. Pat. No. 5,073,448, the disclosure content of which is regarded as part of the present description.

The recording material can also be transparent, for example in the case of projection films.



Compounds of the formula (I) can be incorporated into the material even in the course of manufacture; in papermaking, for example, by addition to the pulp. Another method of use is the spraying of the material with an aqueous solution (or dispersion) of compound(s) of the formula (I), or the addition thereof to the coating.

Coatings for transparent recording materials for projection must not contain any lightscattering particles such as pigments or fillers.

The colour-binding coatings can contain further additives, for example antioxidants, light stabilizers, viscosity improvers, brighteners, biocides and/or antistats.

The coating is usually prepared as follows:



The water-soluble components, for example the binder, are dissolved in water and mixed. The solid components, for example fillers and other additives as already described, are dispersed in this aqueous medium. Dispersion is advantageously brought about with the aid of equipment such as ultrasonic devices, turbine agitators, homogenizers, colloid mills, bead mills, sand mills, high-speed stirrers and the like. A particular advantage of the compounds of the formula (I) is their ease of incorporation into the coating.

As mentioned, the recording materials cover a broad field of use. Compounds of the formula (I) can be employed, for example, in pressure-sensitive copier systems. They can be added to the paper to protect the microencapsulated dye precursors against light and heat, or to the binder of the developer layer for protecting the dyes formed therein.

Photocopier systems with light-sensitive microcapsules which are developed by pressure are described, inter alia, in U.S. Pat. No. 4,416,966; 4,483,912; 4,352,200; 4,535,050; 4,5365,463; 4,551,407; 4,562,137 and 4,608,330; and also in EP-A-139,479; EP-A-162,664; EP-A-164,931; EP-A-237,024; EP-A-237,025 and EP-A-260,129. In all these systems the

compounds of the formula (I) can be added to the colour-accepting layer. Alternatively, the compounds of the formula (I) can be added to the donor layer for protecting the colour formers against light and heat.

The compounds of the formula (I) can also be employed in recording materials which are based on the principle of photopolymerization, photosoftening or the rupture of microcapsules, or when heat-sensitive or photosensitive diazonium salts, leuco dyes with oxidizing agent or colour lactones with Lewis acids are used.

Heat-sensitive recording material exploits the colour-imparting reaction between a colourless or weakly coloured base dye and an organic or inorganic colour developer, the recorded image being produced by heat-induced contact of the two materials. This type of heat-sensitive recording material is very widespread, not only as the recording medium for faxes, computers, etc., but also in many other fields, for example in label printing.

The heat-sensitive recording material according to the present invention is composed of a base, a heat-sensitive colour-forming recording layer on this base, and, optionally, a protective layer on the heat-sensitive, colour-forming recording layer. The heat-sensitive, colour-forming recording layer contains as its principal constituent a colour-imparting compound and a colour-developing compound, and also a compound of the formula (I). If the said protective layer is present, the compound of the formula (I) can also be incorporated into the protective layer.

Heat-sensitive recording materials are described, for example, in JP-A 8-267 915.

Further fields of use are recording materials for dye diffusion transfer printing, thermal wax transfer printing and dot matrix printing, and for use with electrostatic, electrographic, electrophoretic, magnetographic and laser-electrophotographic printers, recorders or plotters. Of the materials mentioned, preference is given to recording materials for dye diffusion transfer printing, as are described, for example, in EP-A-507,734.

The novel recording material preferably contains 1 to 10,000 mg/m², in particular 50 - 2,000 mg/m², of at least one compound of the formula I.



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Compounds of the formula (I) can also be employed in inks, preferably for ink-jet printing, for example those as described in U.S. Pat. No. 5,098,477, the disclosure content of which is regarded as part of the present description. The invention therefore also provides an ink comprising at least one compound of the formula (I) as stabilizer. The inks according to the invention contain at least one dye. In this regard the nature of the ink and the dye dissolved in it and the type of printer used are immaterial.



In many printers a distinction is drawn between those which have a continuous ink jet and "drop-on-demand" printers, in particular double-jet printers. The ink according to the invention can be used for the equipment of all these processes, specifically for printing ink jet printing paper and films.

The inks are in most cases aqueous inks, but they can also be solutions of the dye in an organic solvent or in a melted wax. In most cases aqueous inks still contain water-soluble solvents, for example mono-, di- or tri-ethylene glycols or higher ethylene glycols, propylene glycol, 1,4-butanediol or ethers of such glycols, thiodiglycol, glycerol and ethers and esters thereof, polyglycerol, mono-, di- and tri-ethanolamine, propanolamine, dimethylformamide, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone, 1,3-dimethylimidazolidone, methanol, ethanol, isopropanol, n-propanol, diacetone alcohol, acetone, methyl ethyl ketone or propylene carbonate.



Aqueous inks contain water-soluble dyes such as are also known for dyeing natural fibers. These can, for example, be monoazo, disazo or polyazo dyes, reactive dyes, triphenylmethane dyes, xanthene dyes or phthalocyanine dyes. Examples of these are Food Black 2, C.I. Direct Black 19, C.I. Sulphur Black 1, Acid Red 35, Acid Yellow 23 and copper phthalocyanines, and also Direct Black 38, Direct Black 168, Acid Red 249, Direct Red 227, Direct Yellow 86, Acid Blue 9, Direct Blue 86 and Direct Blue 199.

Aqueous inks can also contain various additives in minor amounts, for example binders, surfactants, biocides, corrosion inhibitors, sequestering agents, pH buffers or conductivity additives. They can also contain water-soluble UV absorbers or other water-soluble light stabilizers. In general, however, the addition, according to the invention, of a stabilizer of the formula I to the ink is adequate.

If the ink is a nonaqueous ink, it is a solution of the dye in an organic solvent or solvent mixture. Examples of solvents used for this purpose are alkyl carbitols, alkylcellosolves,

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dialkylformamides, dialkylacetamides, alcohols, especially alcohols having 1-4 C atoms, acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, diisopropyl ketone, dibutyl ketone, dioxane, ethyl butyrate, ethyl isovalerate, diethyl malonate, diethyl succinate, methyl pelargonate, butyl acetate, triethyl phosphate, ethylglycol acetate, toluene, xylene, tetralin or petroleum fractions. Examples of solid waxes as solvents, which, as an ink, must first be heated, are stearic or palmitic acid.

Inks of this type based on solvents contain dyes soluble therein, for example Solvent Red, Solvent Yellow, Solvent Orange, Solvent Blue, Solvent Green, Solvent Violet, Solvent Brown or Solvent Black. Inks of this type too can also contain further additives, such as are mentioned above for aqueous inks.

The inks according to the invention preferably contain 0.01-30 % by weight, in particular 0.1-20 % by weight, of a compound of the formula (I).

Some of the compounds of the formula I are new compounds. Thus, this invention also pertains to a compound of the formula V

wherein

 R_4 is -(CH₂)_s-COR'₁₅ or -C_pH_{2p}-COR₁₅ or -C_tH_{2t}-COR₁₅, wherein the alkylene moiety C_pH_{2p} is branched alkylene and the alkylene moiety C_tH_{2t} is a straight chain or branched alkylene moiety;

$$R_{15}$$
 is hydroxy, $\left[-O^{-}\frac{1}{r}M^{r+}\right]$, C_1 - C_{20} alkoxy, $-N$
 R_{25} , or a group of the formula IIIa

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$$-Q-z = \begin{bmatrix} O & R_3 & R_2 \\ O & C_m H_{2m} & O \\ R_5 & R_1 & H & K \end{bmatrix}$$
 (IIIa);

R'15 is a group of formula IIIa;

Q is oxygen or -NH-,

Z is a linking group of valency (k+1) and is as a divalent group C_2 - C_{12} alkylene, Q-interrupted C_4 - C_{12} alkylene, phenylene or phenylene-D-phenylene with D being C_1 - C_4 alkylene, O, S, SO or SO₂;

Z as a trivalent group is C_3 - C_{12} alkanetriyl, a trivalent residue of a hexose or a hexitol, a group $(-CH_2)_3C$ - CH_2OH , or a group $-C_aH_{2a}$ - $N(C_bH_{2b}$ -)- C_cH_{2c} -; and

Z as a tetravalent group is a tetravalent residue of a hexose or a hexitol, C₄-C₁₂alkanetetryl, a

group
$$CH_2$$
 or a group CH_2 CH_2 CH_2 CH_3 CH_4 CH_5 CH_5

a, b, c and k independently are 1, 2 or 3,

m is 0 or a number from the range 1-12, preferably 1-6,

p is 1 or 2;

s is 1 or 2;

t is a number from the range 3-12, preferably 3-6;

and all other residues are as defined for formula I if n is 1.

Preferred compounds of the formula V are, within the limits given, as defined for formulae I or IV above.

Compounds of the formula V are also useful as stabilisers for organic material against degradation by light, oxygen and/or heat. Application of these compounds and methods of stabilising are generally as described in GB-A-2322861; examples for organic material which can be stabilized are listed, for example, in GB-A-2319523 from page 15, line 11, until page 20, line 25; possible costabilizers are as listed, for example, in GB-A-2319523 from page 21,

line 16, until page 32, bottom line. Compounds of the formula V are used for this application preferably in an amount of 0.0005 to 5%, based on the weight of the organic material to be stabilised.

Examples for compounds of the formula I to be used within this invention are:

Compound 1^{a)}:

Compound 2:

Compound 3 a):

Compound 4 a):

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Compound 5:

Compound 6 a):

Compound 7 a):

Compound 8:

Compound 9 a):

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Compound 10 a):

Compound 11 a):

Compound 12 a):

Compound 13 a):

Compound 14 a):

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Compound 15 a):

Compound 16 a):

Compound 17 a):

Compound 18 a):

Compound 19:

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Compound 20:

Compound 21 a):

Compound 22:

Compound 23 a):

Compound 24:

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Compound 25 a):

Compound 26 a):

Compound 27 a):

Compound 28:

a) The product may additionally contain minor amounts of other structural isomers in accordance with the substitution at the phenyl ring in 3-position of the benzofuran-2-one. For

example, compound 7 comprises the 2 isomers

The synthetic methods used for the preparation of the benzofuran-2-ones shown above are described e.g. in US Patent 5,516,920.

Example 1

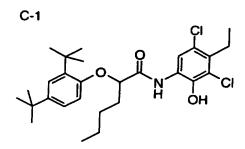
To evaluate compounds of this invention with respect to their ability as interlayer scavengers for oxidised developing agent, three layer photographic test elements are prepared by providing layers in the order indicated on a polyethylene-coated paper support:

Test element 1 (reference sample)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 180 mg.m⁻² of dibutylphtalate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (2) An interlayer containing:
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer containing:
 - 260 mg.m⁻² (based on silver) of an unsensitized silver bromide emulsion
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of magenta-dye-forming coupler M-1
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
 - 2-hydroxy-4,6-dichloro-1,3,5-triazine, potassium salt hardener
 - 7-methyl-5-hydroxy-1,3,8-triazaindolizine antifoggant.

T st element 2 (check sampl)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 272 mg.m⁻² of cyan-dye-forming coupler C-1
 - 180 mg.m⁻² of dibutylphtalate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (2) An interlayer having the same composition as the interlayer of test element 1
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 1.



Test elements 3-8

- (1) A layer having the same composition as the first layer of test element 2
- (2) An interlayer containing
 - 1800 mg.m⁻² of gelatin
 - 0.056x10⁻³ mol.m⁻² of oxidised developer scavenger as indicated in table 1 below
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 1.

The test elements are imagewise exposed through a step wedge with density increment 0.15 and thereafter subjected to the AGFA P-94 developing process.

Within test elements 2-9, cyan dye can only be formed by the wandering of the oxidised developer from the layer in which it is formed (i.e. the uppermost layer) to the bottom layer containing the cyan-dye-forming coupler. The ability of an interlayer scavenger to prevent oxidised developer from diffusing into the bottom layer can thus be assessed by determining the red density at any chosen exposure amount.

The red density at the exposure amount giving a green density of 2 is reported in table 1. The red density in the test element containing no cyan coupler in the bottom layer (test element 1) arises exclusively from the side absorption of the magenta dye in the red part of the visible spectrum.

Table 1

| Test elem nt | Int rlaver | Red d nsity |
|--------------|------------|--------------|
| | int nayer | ned d risity |

| | scavenger | at a green density |
|---------------|------------|--------------------|
| | | of 2 |
| 1 (reference) | none | 0.268 |
| 2 (check) | none | 0.400 |
| 3 | Compound 1 | 0.320 |
| 4 | Compound 2 | 0.278 |
| 5 | Compound 3 | 0.349 |
| 6 | Compound 4 | 0.313 |
| 7 | Compound 5 | 0.327 |
| 8 | Compound 6 | 0.319 |

Any red density inferior to that observed in sample 2 indicates scavenging of the oxidised developer. It is thus clear from the data in table 1 that compounds within the scope of this invention are very effective in preventing the oxidised developer from wandering and forming dye in the wrong layer.

Example 2

Three layer photographic test elements are prepared by providing layers in the order indicated on a polyethylene-coated paper support :

Test element 9 (reference sample)

Same as test element 1 of example 1

Test element 10 (check sample)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 272 mg.m⁻² of cyan-dye-forming coupler C-2
 - 180 mg.m⁻² of dibutylphtalate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (2) An interlayer having the same composition as the interlayer of test element 9
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 9.

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Test elements 11-14

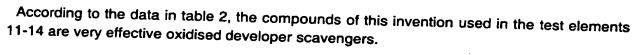
- (1) A layer having the same composition as the first layer of test element 10
- (2) An interlayer containing
 - 1800 mg.m⁻² of gelatin
 - 30 mg.m⁻² of oxidised developer scavenger as indicated in table 2 below
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 9.

The test elements are exposed and processed in the same manner as in example 1.

The red density at the exposure amount giving a green density of 2 is reported in table 2.

Table 2

| Test element | Interlayer | Red density |
|---------------|-------------|--------------------|
| | scavenger | at a green density |
| | | of 2 |
| 9 (reference) | none | 0.264 |
| 10 (check) | none | 0.372 |
| 11 | Compound 7 | 0.284 |
| 12 | Compound 8 | 0.308 |
| 13 | Compound 9 | 0.300 |
| 14 | Compound 24 | 0.302 |



Example 3

Three layer photographic test elements are prepared by providing layers in the order indicated on a polyethylene-coated paper support:

Test element 15 (check sample)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 272 mg.m⁻² of cyan-dye-forming coupler C-2
 - 180 mg.m⁻² of dibutylphtalate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (2) An interlayer containing:
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent

- (3) A photosensitive layer containing:
 - 260 mg.m⁻² of an unsensitized silver bromide emulsion
 - 1800 mg.m⁻² of gelatin
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
 - 2-hydroxy-4,6-dichloro-1,3,5-triazine, sodium salt hardener
 - 7-methyl-5-hydroxy-1,3,8-triazaindolizine antifoggant.

Test elements 16-27

- (1) A layer having the same composition as the first layer of test element 15
- (2) An interlayer containing
 - 1800 mg.m⁻² of gelatin
 - 30 mg.m⁻² of oxidised developer scavenger as indicated in table 3 below
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 15.

The test elements are given a stepped exposure and processed as in example 1.

Cyan dye formation within the above described test elements will again only result from the wandering of the oxidised developer from the photosensitive layer to the layer containing the cyan-dye-forming coupler. The ability of an interlayer scavenger to prevent oxidised developer from diffusing into the bottom layer can thus be assessed by measuring the red density at any given exposure.

As the above described samples contain no dye-forming coupler in the photosensitive layer, there is almost no consumption of the oxidised developer within the latter and the flux of oxidised developer through the interlayer towards the layer containing the cyan coupler is thus markedly increased as compared to the samples of examples 1 and 2.

In table 3, $(D_{red})_{1.35}$ is the red density at the exposure amount obtained behind the 1.35 density step of the step wedge. With the test elements 1-14, this exposure amount gives a green density of about 1.9. The smaller the $(D_{red})_{1.35}$ value, the more effective the scavenging of the oxidised developer.

Table 3

| Table 0 | | | |
|--------------|-------------|--------------------|--|
| Test element | Interlayer | $(D_{red})_{1.35}$ | |
| | Scavenger | | |
| 15 (check) | none | 0.405 | |
| 16 | Compound 7 | 0.282 | |
| 17 | Compound 10 | 0.250 | |
| 18 | Compound 11 | 0.309 | |
| 19 | Compound 12 | 0.292 | |
| 20 | Compound 13 | 0.318 | |
| 21 | Compound 14 | 0.324 | |

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| 22 | Companyed | | |
|----|-------------|----------------|--|
| | Compound 15 | 0.335 | |
| 23 | Compound 16 | 0.300 | |
| 24 | Compound 18 | 0.314 0.335 | |
| 25 | Compound 19 | | |
| 26 | Compound 20 | 0.344 | |
| 27 | Compound 21 | 0.314 | |
| | | U.U.T | |

From the data in table 3, it can be seen again that 3-aryl-3H-benzofuran-2-ones according to this invention exhibit outstanding scavenging ability, as evidenced by much smaller red density values in the test elements 16-27 as compared to the check sample.

Example 4

Three layer photographic test elements are prepared by providing layers in the order indicated on a polyethylene-coated paper support :

T st element 28 (reference sample)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 180 mg.m⁻² of dibutylphtalate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (2) An interlayer containing:
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer containing:
 - 260 mg.m⁻² of an unsensitized silver bromide emulsion
 - 1800 mg.m⁻² of gelatin
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
 - 2-hydroxy-4,6-dichloro-1,3,5-triazine, sodium salt hardener
 - 7-methyl-5-hydroxy-1,3,8-triazaindolizine antifoggant.

Test element 29 (check sample)

Same as test element 15 of example 3 except that the cyan coupler used was C-1 instead of C-2.

Test lements 30-33

- (1) A layer having the same composition as the first layer of test element 29
- (2) An interlayer containing
 - 1800 mg.m⁻² of gelatin
 - Oxidised developer scavenger as indicated in table 4 below
 - 300 mg.m⁻² of tricresylphosphate

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- 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- (3) A photosensitive layer having the same composition as the photosensitive layer of test element 29.

The test elements are given a stepped exposure and processed as in example 1.

In table 4, $(D_{red})_{1.05}$ is the red density at the exposure amount obtained behind the 1.05 density step of the step wedge. For test elements 1-14, this exposure amount gives a green density of about 2.4. The smaller the $(D_{red})_{1.05}$ value, the more effective the scavenging of the oxidised developer.

Table 4

| Test element | Interlayer | Concentration | (D _{red}) _{1.05} |
|----------------|------------|------------------------|-------------------------------------|
| | Scavenger | · | |
| 28 (reference) | none | - | 0.080 |
| 29 (check) | none | • | 0.482 |
| 30 | Compound 7 | 30 mg.m ⁻² | 0.390 |
| 31 | Compound 7 | 60 mg.m ⁻² | 0.313 |
| 32 | Compound 7 | 90 mg.m ⁻² | 0.202 |
| 33 | Compound 7 | 120 mg.m ⁻² | 0.127 |

From the data in table 4, it can be seen that compound 7 according to this invention effectively prevents the formation of cyan dye, and that the Dox scavenging effect increases in proportion to the amount of added compound.

Example 5

Three layer photographic test elements are prepared by providing layers in the order indicated on a polyethylene-coated paper support :

Test element 34 (check sample)

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent.
- (2) A photosensitive layer containing:
 - 260 mg.m⁻² (based on silver) of an unsensitized silver bromide emulsion
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of magenta-dye-forming coupler M-1 (see example 1)
 - 225 mg.m⁻² of the magenta dye light stabiliser S-1 (see below)
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
 - 7-methyl-5-hydroxy-1,3,8-triazaindolizine antifoggant.
- (3) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
 - 2-hydroxy-4,6-dichloro-1,3,5-triazine, potassium salt hardener.

Test elements 35-39

- (1) A layer containing:
 - 1800 mg.m⁻² of gelatin
 - 80 mg.m⁻² of oxidised developer scavenger as indicated in table 5 below
 - 300 mg.m⁻² of tricresylphosphate
 - 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent.
- (2) A photosensitive layer having the same composition as the photosensitive layer of test element 34.
 - (3) A layer containing:
 - 1800 mg.m⁻² of gelatin

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- 80 mg.m⁻² of oxidised developer scavenger as indicated in table 5 below
- 300 mg.m⁻² of tricresylphosphate
- 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- 2-hydroxy-4,6-dichloro-1,3,5-triazine, potassium salt hardener.

The test elements are imagewise exposed through a step wedge with density increment 0.30 and thereafter subjected to the AGFA P-94 developing process.

In order to evaluate them for light fastness, the stepped magenta images obtained in this manner are irradiated through an ultraviolet filter in an Atlas device equiped with a 3500 W Xenon lamp.

In a second experiment, magenta images obtained in the above described way are stored in the dark at 60°C, 95%RH for 72 hours prior to light exposure in the Atlas device.

In all cases the light fastness of the magenta image is evaluated based on the percentage of the residual dye density after 30 kJ/cm² of light exposure (initial density = 1). The results are given in table 5.

Table 5

| Table 3 | | | | |
|-----------------|-------------------------|---|---|--|
| | | Residual dye after 30 kJ.cm ⁻² of Atlas exposure (%) | | |
| Test element | Interlayer Scavenger | no dark storage (60°C, 95% RH) prior to irradiation in the Atlas | 72 h dark storage (60°C, 95% RH) prior to irradiation in the Atlas | |
| 34 (check) | none | 75 | 75 | |
| 35 (comparison) | A-1 | 74 | 60 | |
| 36 (comparison) | A-2 | 71 | 45 | |
| 37 | Compound 7 | 76 | 77 | |
| 38 | Compound 12 | 77 | 74 | |
| 39 | Compound 21 | 75 | 75 | |

From the data in table 5, it can be seen that the oxidised developer scavengers according to this invention are not detrimental at all to the light resistance of the magenta layer, whether the samples are subjected to a preliminary dark storage period at 60°C, 95%RH or not. In contrast, the comparison hydroquinone scavengers A-1 and A-2 clearly impair the light fastness of the magenta image after the samples had been left under a high temperature and humidity for 72 hours.

Exampl 6

Test element 40 is prepared by providing on a polyethylene-coated paper support a light-sensitive silv r halide layer containing:

- 260 mg.m⁻² (based on silver) of an unsensitized silver bromide emulsion
- 5150 mg.m⁻² of gelatin
- 305 mg.m⁻² of magenta-dye-forming compound M-1
- 305 mg.m⁻² of tricresylphosphate
- 2-sulfonate-4,8-diisobutyl-naphtalene, sodium salt surface active agent
- 2-hydroxy-4,6-dichloro-1,3,5-triazine, potassium salt hardener
- 7-methyl-5-hydroxy-1,3,8-triazaindolizine antifoggant

Test elements 41 and 42 are prepared identically to test element 40, except that the emulsion layer additionally contains 30 mg.m⁻² and 75 mg.m⁻² of compound 7, respectively.

The prepared test elements are imagewise exposed through a step wedge with density increment 0.30 and thereafter subjected to the AGFA P-94 developing process.

The stepped magenta images obtained in this manner are irradiated through an ultraviolet filter in an Atlas device equiped with a 3500 W Xenon lamp.

The light fastness of the magenta image is evaluated based on the percentage of the residual dye density after 15 kJ/cm² of light exposure (initial density = 1). The results are given in table 6.

Table 6

| Test element | Benzofuranone | Residual dye after 15 kJ.cm ⁻² of Atlas exposure (%) |
|--------------|--|---|
| 40 (control) | none | 31 |
| 41 | compound 7 (30 mg.m ⁻²) | 48 |
| 42 | compound 7 (75 mg.m ⁻²) | 77 |

As compared to a layer without added benzofuranone, magenta layers containing compound 7 are much more stable to light. Thus, the benzofuranone derivatives according to this invention can also find utility as light stabilisers for magenta dyes derived from pyrazolo:azole couplers.

Claims:

1. Process for preventing migration of the oxidised developer in a colour photographic material from one colour sensitive layer to another by incorporating a compound of the formula I into said material

wherein, if n = 1,

R₁ is naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, each of which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, hydroxy, halogen, amino, C₁-C₄alkylamino, phenylamino or di(C₁-C₄-alkyl)amino, or R₁ is a radical of formula II

$$R_7$$
 R_8
 R_{10}
 R_{11}
(II),

and, if n = 2,

 R_1 is unsubstituted or $C_1\text{-}C_4$ alkyl- or hydroxy-substituted phenylene or naphthylen $\,$; or -R_{12}\text{-}X-R_{13}\text{-} ,

 R_2 , R_3 , R_4 and R_5 are each independently of one another hydrogen, chloro, hydroxy, C_1 - C_{25} -alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 -alkyl)amino, C_1 - C_{25} alkanoyloxy, C_1 - C_{25} alkanoyloxy;

 C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or $N-R_{14}$; C_6 - C_9 cycloalkyl-

carbonyloxy, benzoyloxy or C_1 - C_{12} alkyl-substituted benzoyloxy; or R_2 and R_3 , or R_3 and R_4 , or R_4 and R_5 , together with the linking carbon atoms, form a benzene ring; or R_4 is $-C_mH_{2m}$ - COR_{15} or $-(CH_2)_qOH$ or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of formula III

$$R_{2}$$

$$R_{1}$$

$$R_{16}$$

$$R_{17}$$

$$R_{17}$$

$$R_{18}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

wherein R_1 is as defined above for n = 1;

R₆ is hydrogen or, when R₄ is hydroxy, R₆ can also be C₁-C₂₅alkyl or C₃-C₂₅alkenyl;

 R_7 , R_8 , R_{10} and R_{11} are each independently of one another hydrogen, halogen, hydroxy,

 C_1 - C_{25} alkyl; C_2 - C_{25} alkyl which is interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkoxy;

 C_2 - C_{25} alkoxy which is interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkylthio, C_3 - C_{25} -

alkenyl, C_3 - C_{25} alkenyloxy, C_3 - C_{25} alkynyl, C_3 - C_{25} alkynyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkyl, C_7 - C_9 phenyl-alkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_2 -alka-

noyl; C₃-C₂₅alkanoyl which is interrupted by oxygen, sulfur or N-R₁₄; C₁-C₂₅alkanoyl-

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oxy; C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or $N - R_{14}$; C_1 - C_{25} alka-

noylamino, C₃-C₂₅alkenoyl; C₃-C₂₅alkenoyl which is interrupted by oxygen, sulfur or

N-R₁₄; C₃-C₂₅alkenoyloxy; C₃-C₂₅alkenoyloxy which is interrupted by oxygen, sulfur or

N-R₁₄; C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-

substituted benzoyl; benzoyloxy or C1-C12alkyl-substituted benzoyloxy;

R₁₁, together with the linking carbon atoms, form a benzene ring,

 R_{12} and R_{13} are each independently of the other unsubstituted or C_1 - C_4 alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

 R_{15} is hydroxy, $\left[-0^{-\frac{1}{r}}M^{r+}\right]$, C_1 - C_{20} alkoxy, -N R_{25} , or a group of the formula IIIa

$$-Q-z = \begin{bmatrix} O & R_3 & R_2 \\ O & C_m H_{2m} & O \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

 R_{16} and R_{17} are each independently of the other hydrogen, CF_3 , C_1 - C_{12} alkyl or phenyl, or R_{16} and R_{17} , together with the linking carbon atom, are a C_5 - C_8 cycloalkylidene ring which is unsubstituted or substituted by 1 to 3 C_1 - C_4 alkyl;

 R_{18} and R_{19} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl, R_{20} is hydrogen or C_1 - C_4 alkyl,

R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl; C₂-C₂₅alkyl

which is interrupted by oxygen, sulfur or N-R₁₄; C₇-C₉phenylalkyl which is unsubsti-

tuted or substituted at the phenyl moiety by 1 to 3 C₁-C₄alkyl; C₇-C₂₅phenylalkyl which is interrupted by oxygen, sulfur or $N-R_{14}$ and which is unsubstituted or substituted at the phenyl moiety by 1 to 3 C₁-C₄alkyl, or R₂₀ and R₂₁, together with the linking carbon atoms, form a C₅-C₁₂cycloalkylene ring which is unsubstituted or substituted by 1 to 3 C₁-C₄alkyl; R₂₂ is hydrogen or C₁-C₄alkyl,

R₂₃ is hydrogen, C₁-C₂₅alkanoyl, C₃-C₂₅alkenoyl; C₃-C₂₅alkanoyl which is interrupted by oxygen, sulfur or $N-R_{14}$; C_2-C_{25} alkanoyl which is substituted by a di(C_1-C_6 alkyl)phosphonate group; C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted

R₂₄ and R₂₅ are each independently of the other hydrogen or C₁-C₁₈alkyl,

R₂₆ is hydrogen or C₁-C₈alkyl,

R₂₇ is a direct bond, C₁-C₁₈alkylene; C₂-C₁₈alkylene which is interrupted by oxygen, sulfur or

 $N - R_{14}$; $C_2 - C_{18}$ alkenylene, $C_2 - C_{20}$ alkylidene, $C_7 - C_{20}$ phenylalkylidene, $C_5 - C_8$ cycloalky-

lene, C7-C8bicycloalkylene, unsubstituted or C1-C4alkyl-substituted phenylene,

$$\int_{0}^{\infty}$$
 or \int_{s}^{∞} .

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$$R_{28}$$
 is hydroxy, $\left[-O^{-}\frac{1}{r}M^{r+}\right]$, C_1 - C_{18} alkoxy or $-N$
 R_{26}

R₂₉ is oxygen or -NH-,

R₃₀ is C₁-C₁₈alkyl or phenyl,

R₃₁ is hydrogen or C₁-C₁₈alkyl,

M is an r-valent metal cation,

Q is oxygen or -NH-,

X is a direct bond, oxygen, sulfur or -NR₃₁-,

Z is a linking group of valency (k+1) and is as a divalent group C_2 - C_{12} alkylene, Q-interrupted C_4 - C_{12} alkylene, phenylene or phenylene-D-phenylene with D being C_1 - C_4 alkylene, O, S, SO or SO₂;

Z as a trivalent group is C_3 - C_{12} alkanetriyl, a trivalent residue of a hexose or a hexitol, a group $(-CH_2)_3C$ - CH_2OH , or a group $-C_aH_{2a}$ - $N(C_bH_{2b}$ -)- C_cH_{2c} -; and

Z as a tetravalent group is a tetravalent residue of a hexose or a hexitol, C₄-C₁₂alkanetetryl, a

a, b, c and k independently are 1, 2 or 3,

m is 0 or a number from the range 1-12, preferably 1-6,

n is 1 or 2.

q is 1, 2, 3, 4, 5 or 6,

r is 1, 2 or 3, and

s is 0, 1 or 2;

provided that, when R_7 is hydroxy, alkanoyloxy or alkanoyloxy interrupted by O, S or N(R_{14}) and R_9 is hydrogen, R_{10} is not identical with R_4 ; and when R_9 is hydroxy, alkanoyloxy or alkanoyloxy interrupted by O, S or N(R_{14}) and R_7 is hydrogen, R_8 is not identical with R_4 .

2. Process according to claim 1, wherein in the compound of formula I R_2 , R_3 and R_5 , independently, are H, Cl, hydroxy, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; C_1 - C_{18} alkoxy, C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkenoyloxy; and where

 R_4 is CI, hydroxy, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; C_1 - C_{18} alkoxy, C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkenoyloxy or is a group - C_mH_{2m} - COR_{15} , or where R_3 , R_5 and R_6 are H, R_4 may be a residue of formula III, or where R_8 or R_{10} are other than H, R_4 may also be hydrogen;

R₆ is H,

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently are H, halogen, hydroxy, C_1 - C_{25} alkyl, O interrupted C_2 - C_{25} alkyl; C_1 - C_{25} alkoxy, O interrupted C_2 - C_{25} alkoxy, C_3 - C_{25} alkenyl, C_3 - C_{25} alkenyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl substituted phenoxy; unsubstituted or C_1 - C_4 alkyl substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di- $(C_1$ - C_4 -alkyl)amino, C_1 - C_2 5alkanoyl; C_1 - C_2 5alkanoyloxy; C_6 - C_9 cycloalkylcarbonyloxy, benzoyl or C_1 - C_{12} alkyl-substituted benzoyl; benzoyloxy or C_1 -

C₁₂alkyl substituted benzoyloxy;
$$-O-\overset{R_{18}}{C}-C-R_{15} \text{ or } -O-\overset{R_{20}}{C}-C-O-R_{23} \text{ , or } R_{19}$$

where in formula II R_7 and R_8 or R_8 and R_{11} together with the carbon atoms, they are bonded to, form a phenyl ring;

 R_{15} is C_1 - C_{18} alkoxy or N or a group of formula IIIa; R_{25}

$$-Q-z = \begin{bmatrix} O & R_3 & R_2 \\ O & C_m H_{2m} & O \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

 R_{16} and R_{17} independently are H, CF_3 , C_1 - C_{12} alkyl or phenyl; or R_{16} and R_{17} together with the bonding carbon atom form an unsubstituted or 1-3 C_1 - C_4 alkyl-substituted C_5 -

C₈cycloalkylidene ring;

R₁₈ and R₁₉ independently are H, C₁-C₄ alkyl or phenyl;

R₂₀ is H or C₁-C₄alkyl;

 R_{21} is H, unsubstituted or C_1 - C_4 alkyl substituted phenyl; C_1 - C_{25} alkyl, unsubstituted or on the phenyl ring 1-3 C_1 - C_4 alkyl-substituted C_7 - C_9 phenylalkyl;

R₂₂ is H or C₁-C₄alkyl;

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 R_{23} is H, C_1 - C_{25} alkanoyl, C_3 - C_{25} alkenoyl; di(C_1 - C_6 alkyl)phosphonate-substituted C_2 - C_{25} alkanoyl; C_6 - C_9 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1 - C_{12} alkyl-substituted

benzoyl;
$$O = C - C_3 H_{23} - C - C_4 H_{23} - C - C_5 - C$$

 R_{24} and R_{25} independently are H or C_{1} - C_{18} alkyl;

R₂₆ is H or C₁-C₈alkyl;

R₂₇ is a direct bond, C₁-C₁₈alkylen, C₂-C₁₈alkenylen, C₇-C₂₀phenylalkyliden, C₅-

C₀cycloalkylen, unsubstituted or C₁-C₄alkyl-substituted phenylene, or

R₂₉ is O or -NH-;

R₃₀ C₁-C₁₈alkyl or phenyl:

M a metal cation of the valency r;

X a direct bond, O, S or -NR₃₁-;

n 1 or 2;

m is a number from the range 1-8;

q 1, 2, 3, 4, 5 or 6;

r 1, 2 or 3; and

s is 0, 1 or 2.

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3. Process according to claim 1 wherein the compound of formula I corresponds to the formula IV

wherein

R₂ is H or C₁-C₂₀alkyl;

R₃ is H or C₁-C₁₈alkyl;

R₄ is C₁-C₈alkyl, H, C₁-C₆alkoxy or a group -C_mH_{2m}-COR₁₅ or a group of the formula III

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

R₅ is H or C₁-C₁₈alkyl;

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently are H, OH, chloro, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, di(C_1 - C_4 alkyl)amino, phenyl, C_2 - C_{18} alkanoyloxy, C_3 - C_{18} -alkoxycarbonylalkoxy or

$$-O - \begin{matrix} R_{20} & R_{21} \\ -C & C - C - O - R_{23} \\ H & R_{22} \end{matrix};$$

especially wherein at least 2 of the residues R7, R8, R9, R10, R11 are H;

R₁₅ is C₁-C₁₈alkoxy or a group of the formula IIIa

$$-Q-z = \begin{bmatrix} O & R_3 & R_2 \\ O & C_m H_{2m} & O \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

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 R_{16} and R_{17} independently are H, C_1 - C_{12} alkyl or phenyl; or R_{16} and R_{17} together with the bonding carbon atom form a C_5 - C_8 cycloalkylidene ring;

 R_{20} , R_{21} and R_{22} independently are H or $C_1\text{-}C_4$ alkyl;

R₂₆ is C₁-C₄alkyl;

Q is oxygen;

Z is C2-C12alkylene;

k is 1;

m is 1, 2, 3, 4, 5 or 6 and

s is 0, 1 or 2.

4. Process according to claim 3 wherein in the compound of formula IV

R2 is C1-C20alkyl;

R₃ is H or C₁-C₁₈alkyl;

 R_4 is C_1 - C_6 alkoxy or a group - C_mH_{2m} - COR_{15} or a group of the formula III

$$R_{2}$$

$$R_{16}$$

$$R_{16}$$

$$R_{17}$$

$$R_{17}$$

$$R_{18}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

$$R_{19}$$

R₅ is H or C₁-C₁₈alkyl;

R₇ and R₉ independently are H, chloro, C₁-C₁₈alkyl;

 R_8 , R_{10} and R_{11} independently are H, OH, chloro, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, di(C_1 -

R₁₅ is C₁-C₁₈alkoxy or a group of the formula IIIa

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$$-Q-Z = \begin{bmatrix} Q & R_3 & R_2 \\ Q & C_m H_{2m} & Q \\ R_5 & R_1 & H \end{bmatrix}$$

(IIIa);

R₂₀, R₂₁ and R₂₂ are H;

$$H_3C$$
 CH_3
 CH_3

R₂₆ is C₁-C₄alkyl;

Q is oxygen;

Z is C₂-C₁₂alkylene;

k is 1;

m is 1, 2, 3, 4, 5 or 6 and

s is 0, 1 or 2.

5. Process according to claim 3 where in the compound of formula IV R_7 is H and R_9 is H or methyl and wherein R_2 , R_3 , R_4 , R_5 , R_6 , R_8 , R_9 , R_{10} , and R_{11} together contain at least 3 carbon atoms.

6. Process according to claim 3 wherein in the compound of formula IV, R_4 is C_1 - C_6 alkyl, especially tertiary C_4 - C_6 alkyl, or a group - C_mH_{2m} - COR_{15} or a group of the formula III.

- 7. Process according to claim 1, wherein the compound of formula I is incorporated into the colour photographic material in an amount from 10 to 1000 mg/m².
- 8. Process according to claim 1, wherein the compound of formula I is concentrated in one or more interlayers separating the light sensitive layers of the colour photographic material.
- 9. Use of a compound of the formula I according to claim 1 as a scavenger for the oxidized developer in a colour photographic material.
- 10. A colour photographic material containing a compound of the formula IV

wherein

R₂ is H or C₁-C₂₀alkyl;

R₃ is H or C₁-C₁₈alkyl;

 R_4 is C_1 - C_8 alkyl, C_1 - C_6 alkoxy or a group - C_mH_{2m} - COR_{15} or a group of the formula III

$$R_2$$
 R_{16}
 R_{17}
 R_{16}
 R_{17}
 R_{17}
 R_{18}
 R_{18}
 R_{19}
 R_{1

R₅ is H or C₁-C₁₈alkyl;

 R_7 and R_9 independently are H, chloro, $C_1\text{-}C_{18}$ alkyl or phenyl;

 R_8 , R_{10} and R_{11} independently are H, OH, chloro, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, di(C_1 - C_4 alkyl)amino, phenyl, C_2 - C_{18} alkanoyloxy, C_3 - C_{18} -alkoxycarbonylalkoxy or

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R₁₅ is C₁-C₁₈alkoxy or a group of the formula IIIa

$$-Q-Z = \begin{bmatrix} Q & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\$$

 R_{16} and R_{17} independently are H, C_1 - C_{12} alkyl or phenyl; or R_{16} and R_{17} together with the bonding carbon atom form a C_5 - C_8 cycloalkylidene ring;

 R_{20} , R_{21} and R_{22} independently are H or $C_1\text{-}C_4$ alkyl;

R₂₆ is C₁-C₄alkyl;

Q is oxygen;

Z is C2-C12alkylene;

k is 1;

m is 1, 2, 3, 4, 5 or 6 and

s is 0, 1 or 2.

11. Use of a compound of the formula IV according to claim 11 as an additive in a colour photographic material.

12. Compound of the formula V:
$$R_3 = R_5 = R_7 = R_{10}$$
 (V),
$$R_4 = R_8 = R_{11}$$

wherein

 R_4 is -(CH₂)_s-COR'₁₅ or -C_pH_{2p}-COR₁₅ or -C_tH_{2t}-COR₁₅, wherein the alkylene moiety C_pH_{2p} is branched alkylene and the alkylene moiety C_tH_{2t} is a straight chain or branched alkylene moiety;

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 R_{15} is hydroxy, $\left[-0^{-\frac{1}{r}}M^{f+}\right]$, C_1 - C_{20} alkoxy, -N R_{25} , or a group of the formula IIIa

$$-Q-z = \begin{bmatrix} Q & R_3 & R_2 \\ Q & C_m H_{2m} & Q \\ R_5 & R_1 & H \end{bmatrix}$$
 (IIIa);

R'15 is a group of formula IIIa;

Q is oxygen or -NH-,

Z is a linking group of valency (k+1) and is as a divalent group C_2 - C_{12} alkylene, Q-interrupted C_4 - C_{12} alkylene, phenylene or phenylene-D-phenylene with D being C_1 - C_4 alkylene, O, S, SO or SO₂;

Z as a trivalent group is C_3 - C_{12} alkanetriyl, a trivalent residue of a hexose or a hexitol, a group $(-CH_2)_3C-CH_2OH$, or a group $-C_aH_{2a}-N(C_bH_{2b}-)-C_cH_{2c}-$; and

Z as a tetravalent group is a tetravalent residue of a hexose or a hexitol, C₄-C₁₂alkanetetryl, a

a, b, c and k independently are 1, 2 or 3,

m is 0 or a number from the range 1-12, preferably 1-6,

p is 1 or 2;

s is 1 or 2;

t is a number from the range 3-12, preferably 3-6;

and all other residues are as defined in claim 1 for formula I if n is 1.

13. Use of a compound of the formula V according to claim 14 as stabilizer for organic material against deterioration by light, oxygen and/or heat.

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Abstract

A colour photographic material is described containing a compound of the formula I

wherein, if n = 1,

 R_1 is, inter alia, a radical of formula II

and, if n = 2,

 R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxy-substituted phenylene or naphthylene; or $-R_{12}$ -X- R_{13} -, and other residues are as defined in claim 1. The compound of the formula I is effective as scavenger of the oxidised form of the developer (Dox scavenger), especially when contained in an interlayer between light sensitive layers. Selected compounds of this class can also be used as additives, for example as dye stabilizer, in colour photographic materials.

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